CHEMICAL TECHNOLOGY AND ANALYSIS

OF

OILS, FATS, AND WAXES

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BY

DR. J. LEWKOWITSCH, M.A., F.I.C.

CONSULTING AND ANALYTICAL CHEMIST, AND CHEMICAL ENGINEER
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,, 138 ,, 12 from bottom, *for* V. *read* VI.
,, 256, between line 7 and 8 from top, *insert* Rattlesnake . . . 105·6.
,, 256, line 8 from top, *add in third column* Semi-drying fats.
,, 256 ,, 11 ,, *delete* Non-drying fats.
,, 256 ,, 19 ,, *add in third column* Non-drying fats.
,, 257 ,, 14 from bottom, *for* insoluble *read* soluble.
,, 268 ,, 3 ,, *for* Acetic Acid *read* Water.
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,, 506 ,, 5 ,, *for* Saubohnenfelt *read* Saubohnenfett.

CHAPTER XIII

COMMERCIAL PREPARATION OF OILS, FATS, AND WAXES

Operations having for their object the preparation of oils, fats, and waxes date back to the remotest times in the history of mankind. Hence the technical appliances used for their production range from the simplest contrivances up to the very elaborate machinery in vogue at present. Some of the oldest appliances still survive to-day, such as the extremely primitive methods employed in the production of palm oil, the expression of olives, the collecting of carnaüba wax, etc. No doubt, the first supplies of vegetable oils and fats were obtained from fruits, such as those of the palm and olive trees. The oils were recovered in an exceedingly crude fashion, either by storing the fruits for some time in holes in the ground, when fermentation of the mass set in and the oil rose to the surface, or by boiling the fruit in water.

An advance in the manufacture was reached with the expression of oils from fruits in some kind of a rough press, exemplified by packing the fruit into sacks, and covering these with boards weighted by stones. A further stage was marked by the production of vegetable oils from oleaginous seeds; these were originally ground up between stones, as is still being done nowadays in East India.

Since oils and fats are obtainable in all countries of the world, it will be readily understood that even the crudest and oldest methods are still in existence. The consideration of these modes of manufacture lies beyond the scope of this work. Nor is it intended to give an exhaustive survey of the subject and describe in detail the more recent manufacturing operations. We shall therefore only briefly glance at the most advanced technical processes and appliances used in large scale operations.

The processes employed for the production of vegetable oils and fats divide themselves naturally into two classes:—(1) The recovery of oils by expression, and (2) the recovery of oils by extraction with volatile solvents.

(1) *The Recovery of Oils by Expression*

This branch of industry has emancipated itself from the early primitive methods through the invention of the hydraulic press and of the accumulator, and has thereby reached the very complete system in vogue nowadays in the best equipped establishments. The machinery required for the preliminary treatment of the fruit or seed will naturally vary with each particular kind of fruit or seed; thus the preparatory operations for laying bare the fat-containing cells of cocoa nuts naturally differ from those necessary in the case of linseed.

A description of the special methods used in the production of each individual oil and fat will be given in the following chapter. Here it must suffice to glance at the modern methods of preparing, crushing, and expressing the oleaginous seeds, as carried out in the "Anglo-American" system of seed crushing.

The seeds or kernels are freed from gross mechanical impurities such as stones, nails, and sand by sieves—in some cases assisted by magnetic separators—and then converted into a pulpy mass or meal by grinding or crushing between stones in edge-runners, or by passing through rollers, such as the Anglo-American five-roller machine, or by comminuting in a disintegrator. Since the catalogues and advertisements of the engineering firms who make a speciality of this class of machinery supply excellent illustrations, it is not deemed necessary to reproduce them here, it being my intention to lay in this work greater emphasis on the chemical technology and general principles of the industries than on a detailed description of the machinery[1] and the manufacturing operations.

The suitably comminuted mass, forming a more or less coarse powder, "meal," is either expressed in this state, or subjected to preliminary heating, the latter depending on the quality of the product to be manufactured. Thus, for the preparation of edible oils, the mass is packed into bags and expressed in hydraulic presses *in the cold*, under a pressure of 300 atmospheres and more (equalling a pressure of two tons or more to the square inch), so that the oil may exude readily (*salad oils*, *cold-drawn oils*, *cold-pressed oils*). Under these conditions the oils dissolve the smallest amount of colouring matters, and suffer in the least degree as regards quality. Obviously only a portion of the oil contained in the fruits or seed is obtained in this manner; a further quantity is gained by expression at a somewhat elevated temperature, which is reached by warming the seed previous to expression. The quality of the oil naturally suffers when expressed in the hot, more of the extractive substances being dissolved and intermixed with the oil. The taste also suffers; the oil thus obtained is hardly suitable for edible purposes and is chiefly used for manufacturing purposes. The oil which is retained by the press cakes can only be recovered by again comminuting the press cakes and subjecting the meal so obtained to a further expression.

In the case of oleaginous seeds of somewhat low value, the aim is to express in one operation the largest possible quantity of oil. Hence the broken seed is generally warmed in a steam-jacketted kettle, fitted

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[1] Cp. Lewkowitsch, Cantor Lectures on "Oils and Fats: their Uses and Applications," *Journ. Soc. Arts*, 1904.

with a mixing gear, by passing steam into the jacket, and sending at the same time some steam by a rose, fixed inside the kettle, into the mass whilst it is being agitated. The assumption that the albuminous mass is thereby coagulated hardly holds good, the object being merely to warm the seed to a higher temperature and at the same time to moisten it, so that the cells part more freely with the imprisoned oil.

The heated meal is then delivered through a measuring box, which is combined with an automatic moulding machine, into bags or open cloths, so that the preliminarily pressed cakes can be put into the hydraulic press, in which the meal is subjected to high pressure. This consists in the Anglo-American type of press, of an open press fitted with a number of iron press plates (from 10 to 16) between which the cakes are inserted by hand. The hydraulic ram then compresses the cakes, whilst the exuding oil flows down the sides into a tank below. After releasing the pressure, the hot cakes are taken out; the edges, which are naturally richer in oil than the bulk, and hence

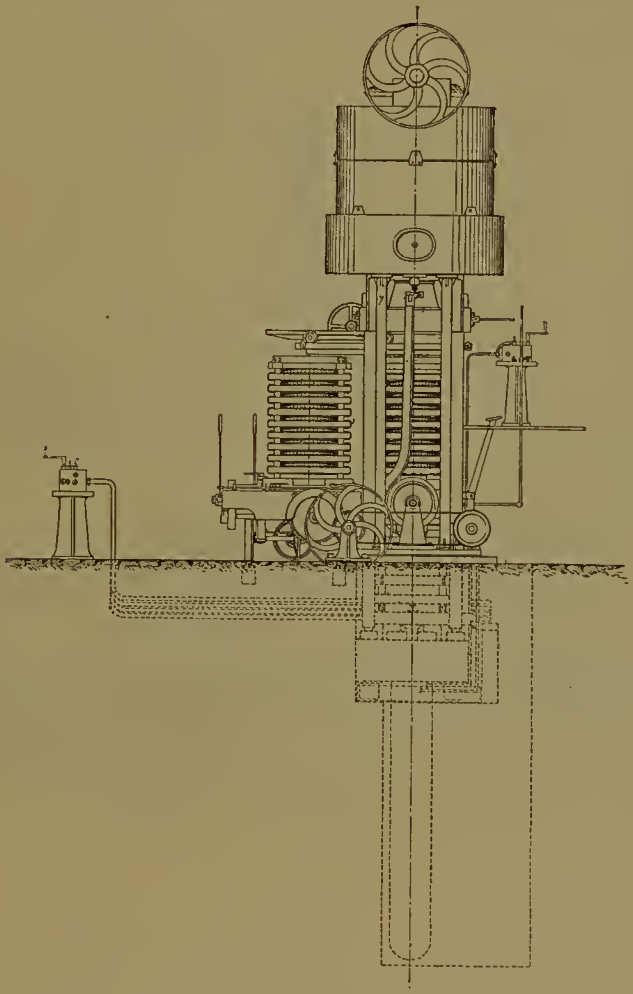

Fig. 54.

are soft and friable, are trimmed off in a paring machine. In those cases where the seeds contain large amounts of oil, exceeding 40 per cent (palm kernels, cocoa nuts, castor seeds), it is necessary to repeat the process of expression. This is done by breaking up the cakes in a cake-breaking machine, reducing them to meal, and subjecting the latter to a second expression in the manner described already.

In the case of those seeds which contain more than 40 per cent of oil, the first expression in bags leads to difficulties, as the oily meal causes "spueing," *i.e.* the meal exudes and escapes from the presses.

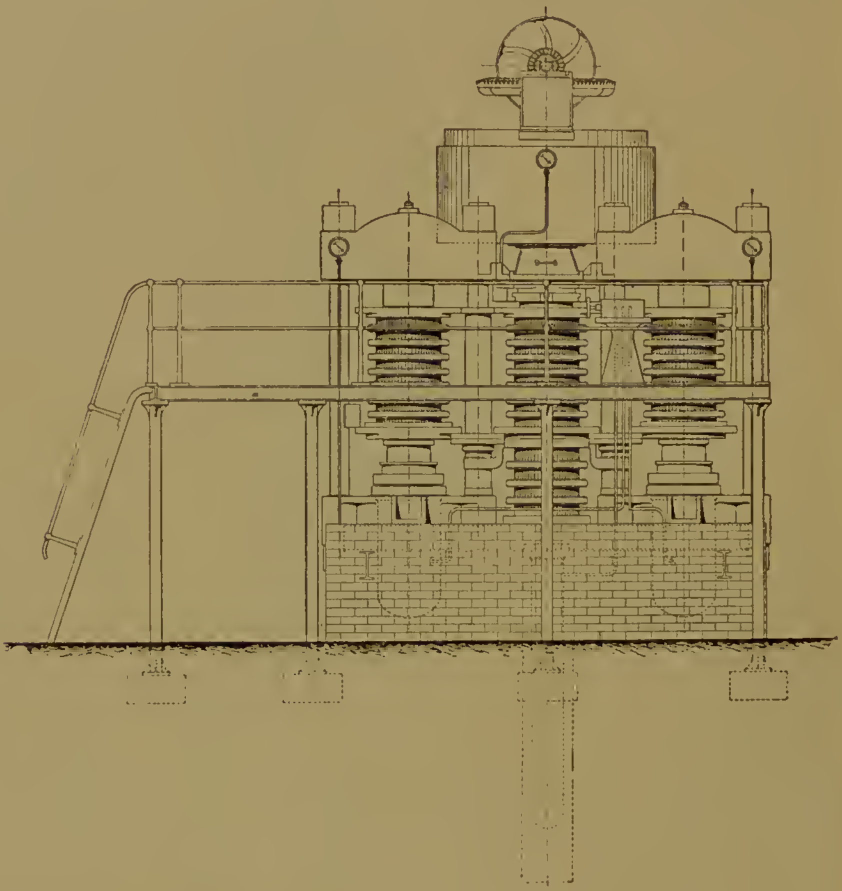

Fig. 55.

Hence in modern installations the first expression of these seeds is carried out in a "clodding" press. This consists of a hydraulic press provided with a circular box or cage into which the meal is filled. The box is either constructed of metal staves (vertical steel bars), held together by a number of steel rings, or consists of one cylinder with perforations. These presses, generally worked in sets of two, or three, or more, have a seed kettle fixed on the top of the press (see Figs. 54 and 55); the kettle is provided with an opening or openings, corresponding to the chamber or chambers in the heads of the press or presses. These chambers can be closed at the top and bottom by slides, actuated by levers, and are designed to contain so much meal as is required to form one cake. The measured charge of meal is then allowed to fall into the press box and covered with a circular metal plate. This operation is repeated until the press is full, when hydraulic pressure is applied, and a ram forces the box against a sliding block at the head of the press. The oil exudes, and the meal is pressed into circular cakes ready for the second expression. After releasing the pressure, and removing the sliding block, the cakes are forced out by the hydraulic ram. They are then broken into meal and subjected to a second expression in the Anglo-American hydraulic press described above.

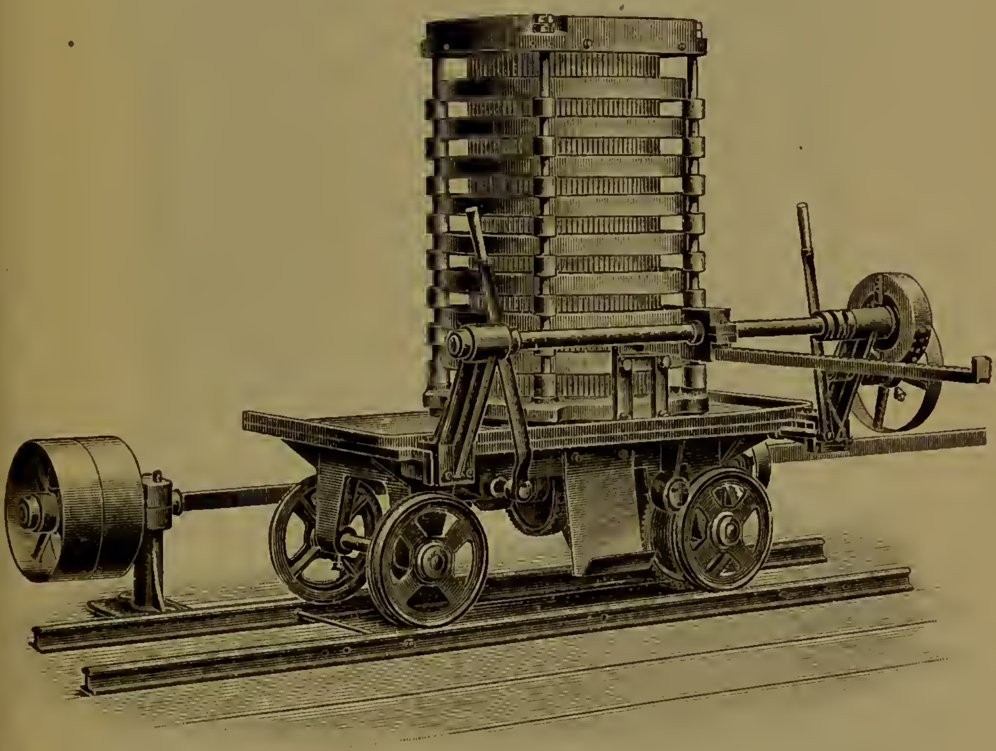

Fig. 56.

Modern improvements in the mechanical part of the process dispenses even for the second expression with the open Anglo-American press. The finishing presses are made of the same type as the press in which the first expression is carried out, and by making the press cages removable, the pressing operation can be made a practically continuous one. These cages can either be transported by means of a power-driven carriage (see Fig. 56) to the finishing presses, or if one preliminary press is combined with two finishing presses to a battery, the cages can be conveyed into the adjoining finishing press by a swinging arrangement (see Figs. 57 and 58), its place being filled immediately by a charged cage, or by a cage containing finished cakes, so that, with the exception of the time required for withdrawing the pressing cages, and replacing them, the work goes on practically continuously. Further advantages are offered by these presses in that the cakes require no paring, and that great saving of press cloths in comparison with the open plate process of the Anglo-American system is effected.

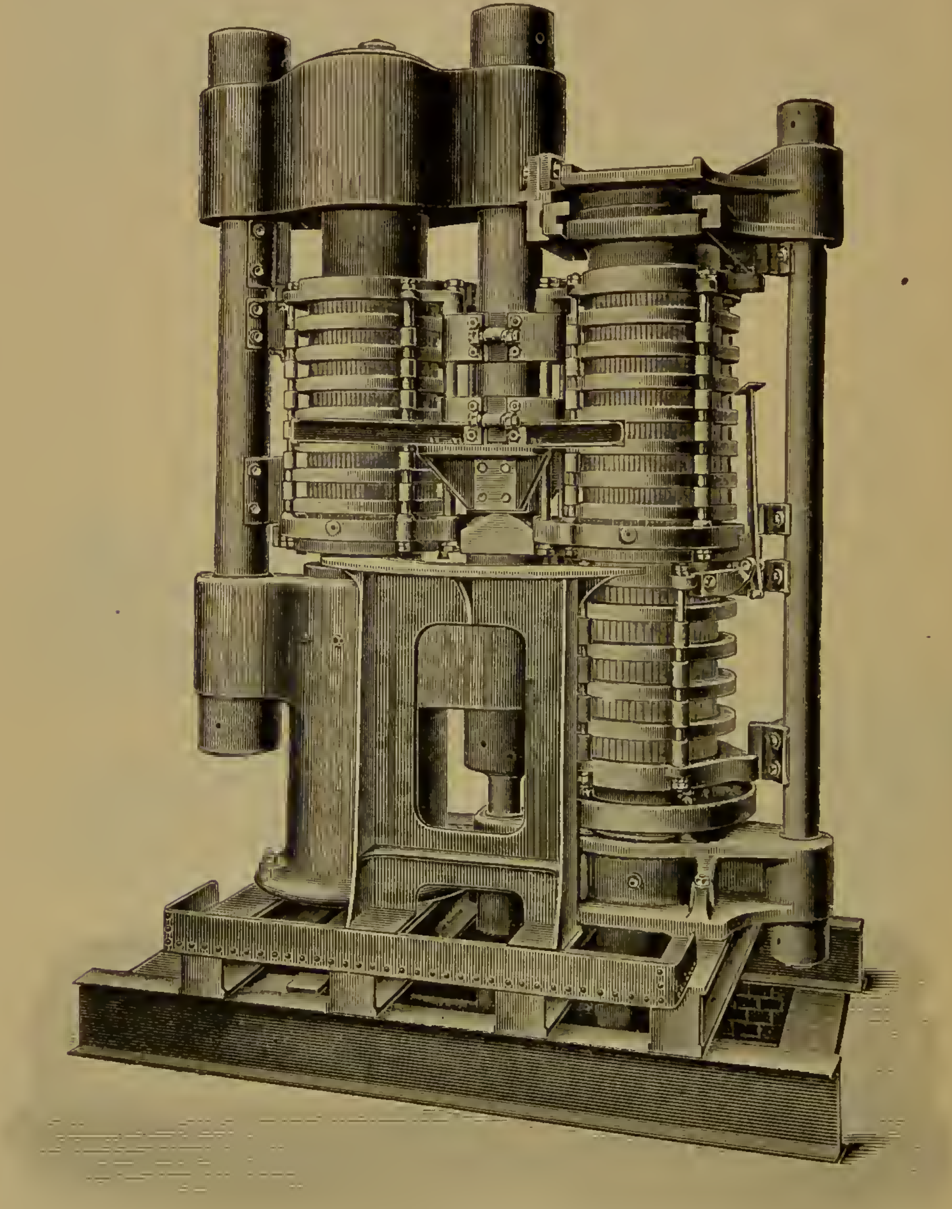

Fig. 57.[1]

The analytical control of the technical process confines itself chiefly to the determination of the proportion of oil or fat contained in the raw material—oleaginous seeds—and the determination of the oil left in the expressed cakes. For the estimation, quantities of not less than 100 grms. should be used.

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[1] The illustrations Figs. 54-58 have been engraved from drawings and photographs kindly lent by Messrs. Greenwood and Batley, Leeds.

The sample is prepared for analysis by disintegrating it carefully in a suitable manner, say by means of a cake-mill or coffee-grinder,[1] and exhausting it with ether or petroleum ether, or carbon tetrachloride,[2] using any of the extracting apparatus described (chap. iv. p. 148). The disintegration of the seeds requires great care, as otherwise considerable quantities of oil or fat may remain in the meal. The breaking up of the cells which occlude the oil or fat is frequently best assisted by grinding with ignited sand, which offers the double advantage of breaking the cells more completely than is done by mere pounding in a mortar and of presenting a large surface to the extracting solvent. In the case of seeds containing large quantities of oils and fats it is advisable to first break up the mass roughly and to extract a portion only of the oil or fat, then to triturate the partially extracted mass with sand and finally exhaust completely. This especially applies to copra, palm kernels, and generally to all seeds containing more than 50 per cent of oil or fat.

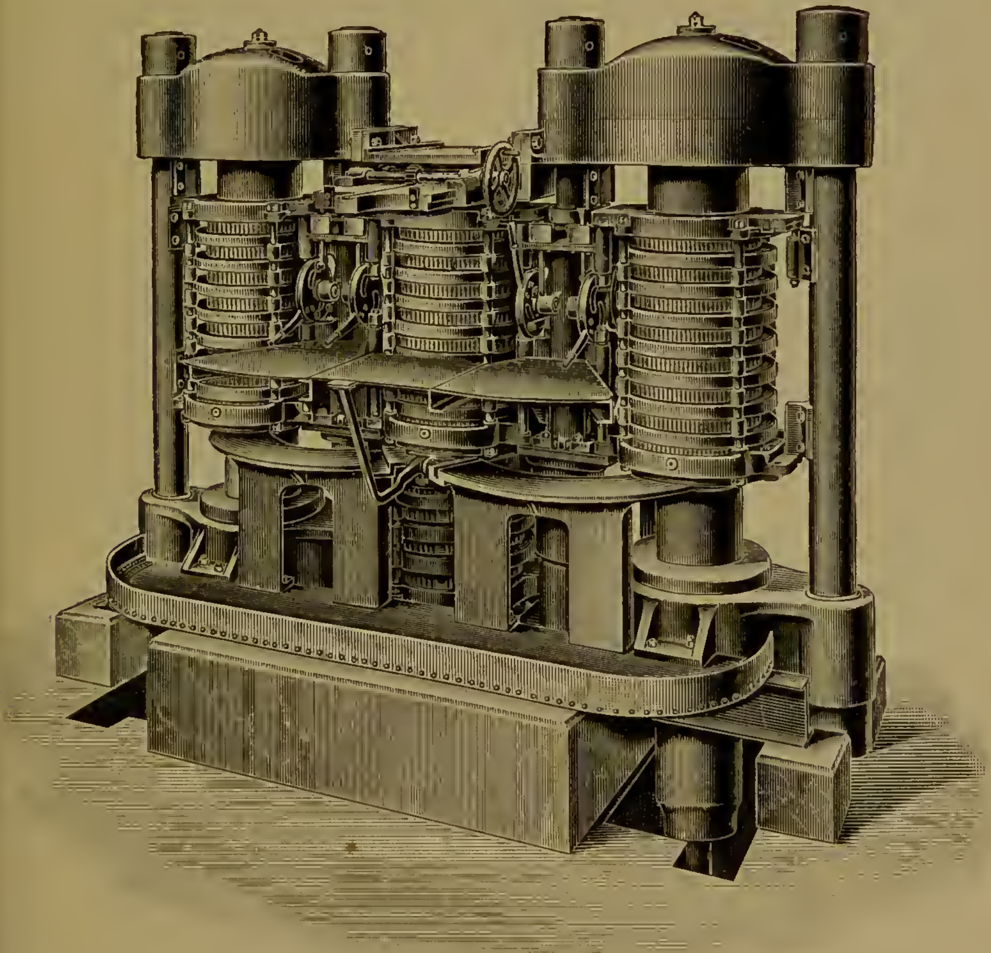

Fig. 58.

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[1] With regard to errors caused by deviating from these directions, cp. *Journ. Soc. Chem. Ind.* 1895, 447.

[2] Bilteryst, *Bull. de l'Assoc. Belge.* 1897 (10), 406.

If ether is employed it is necessary to dry the material prior to extraction, moist seeds or cakes being apt to yield to the ether non-fatty substances. The ether should also be purified; this is best done by washing with water in order to remove any alcohol, then drying over calcium chloride, and distilling off; finally, the ether is distilled over metallic sodium in order to get rid of the last traces of water and alcohol.

The drying of seeds or cakes containing drying oils, such as linseed and linseed cake, requires some care; if the material has been dried at too high a temperature, or for too long a period, the drying oils refuse to pass readily into solution. This fact is clearly brought out by some experiments recorded in the following table due to *Klopsch*:[1]—

Linseed Cake.	Oil. Per cent.
Dried 3 hours at 94°-96° C. gave . .	8·97
Dried 6 hours at 100° C. gave . . .	8·55
Dried 12 hours at 94°-96° C. gave . .	7·89

If the cakes have been dried at too high a temperature, brown resinous extracts are obtained. An analysis can therefore only be looked upon as correct if the extract has the appearance of a fresh, clear oil.

If petroleum ether or carbon tetrachloride be used as solvent, the drying of the material may be omitted (*Nördlinger*, *Bilteryst*).

In special cases the examination of the extracted oil is required; the microscopical examination of the meal will in such cases greatly assist the chemical tests.

A large number of analyses of seeds and oil-cakes have been published by various observers.[2] These naturally fall outside the scope of this work. I will therefore quote only some analyses by *Nördlinger*[3] as throwing some light on the proportion of neutral oil to free fatty acids.

Seeds	100 parts contain		Free Fatty Acids in Total Fat.
	Free Fatty Acids.	Total Fat.	Per cent.
Rape (*Brassica rapa*) . . .	0·42	37·75	1·10
Cabbage (*Brassica campestris*) . .	0·32	41·22	0·77
Poppy (*Papaver somniferum*) . .	3·20	46·90	6·66
Earthnut (*Arachis hypogæa*)—			
(*a*) Seed	1·91	46·09	4·15
(*b*) Husks	1·91	4·43	43·10
Sesamé (*Sesamum orientale*) . .	2·21	51·59	4·59
Castor (*Ricinus communis*) . .	1·21	46·32	2·52
Palm nut (*Elæis guineensis*) with 6 per cent husks	4·19	49·16	8·53
Copra (*Cocos nucifera*) . . .	2·98	67·40	4·42

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[1] *Zeitsch. analyt. Chem.* 1888, 452.

[2] Cp. König. *Die menschlichen Nahrungs- und Genussmittel.*

[3] *Journ. Soc. Chem. Ind.* 1890, 422.

Cakes.	Number of Samples.	100 parts contain		Free Fatty Acids in Total Fat.
		Free Fatty Acids.	Total Fat.	
				Per cent.
Rape	6	0·93	8·81	10·55
Poppy seed	10	5·66	9·63	58·89
Earthnut (Arachis)	20	1·42	7·65	18·62
Sesamé	15	6·15	15·44	40·29
Palm nut	38	1·47	10·39	14·28
Cocoa nut	5	1·31	13·11	10·51
Linseed	2	0·75	8·81	9·75
Castor	10	1·27	6·53	20·07

The total fat was obtained by extraction with petroleum ether, and the free fatty acids were titrated with alkali and calculated to oleic acid.

The ratio of total fat to fatty acids is not necessarily the same in the cakes as in the expressed oils. Thus the "first expressed" oils ("salad oils") contain far less free fatty acids than the total fat in the seeds. Consequently more fatty acids remain in the cakes. The oils from the second and third pressing are richer in fatty acids, but still a large portion thereof remains behind in the cakes.

The following example will illustrate this.

100 Kg. of Poppy Seed yielded	Oil. Per cent.	Containing Free Fatty Acids. Per cent.
When extracted with solvents	46·9	6·82
When expressed—(*a*) Salad oil	39·0	1·92
(*b*) Commercial oil	2·5	15·37
There remained in the cakes	5·4	38·32

The action of enzymes on the neutral glycerides (chap. i. p. 23) undoubtedly plays some part in the production of free fatty acids.

Dyer and *Gilbard*[1] have shown that oil extracted from freshly made linseed cakes contained no free fatty acid; on the other hand, the proportion of free acids increased when the cakes had "heated" or become mouldy in storing. In a further paper[2] these chemists give a large number of determinations of free fatty acids in linseed cakes; in 116 freshly made cakes the oil contained only about 3 per cent of free fatty acids. As a rule, impure cakes show a higher acidity than pure cakes, and when high acidity is found in pure cakes

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[1] *Journ. Soc. Chem. Ind.* 1893, 8.

[2] *Ibid.* 1896, 288; *Analyst*, 1895, 214.

it is probably due to bad condition, such as that produced by "heating" or mouldiness. The reader must be referred to the original paper for the analyses of linseed, rape, arachis (ground nut), and Niger seed cakes; here I can only quote figures relating to uncrushed seeds.[1]

Uncrushed Seeds.	Moisture. Per cent.	Oil. Per cent.	Fatty Acids in 100 parts of Oil.	
Linseed (13 samples)	6·3	39·7	1·30	
Cotton seed (6 samples)	9·8	21·3	7·4	3·6 lowest 12·6 highest
Rape seed (4 samples)	5·8	39·5	0·81	0·15 lowest 1·15 highest
Ravison rape (6 samples)	7·7	25·4	0·90	0·50 lowest 1·87 highest
Jamba rape (2 samples)	7·1	25·7	2·4	
Niger seed	7·3	38·0	0·9	
Sunflower seed	6·2	29·2	1·9	

Emmerling[2] found in the examination of palm kernel cakes the following changes as regards the proportion of free fatty acids in the fat:—

	Free Fatty Acids in 100 parts of Fat.		
	I.	II.	III.
Fresh cakes	14·35	16·14	20·50
Cakes stored two years in the dark	26·44	40·61	...
,, ,, ,, light	...	...	86·08

(2) *Extraction by Means of Volatile Solvents*

From the above given analyses of cakes it will be seen that considerable proportions of oil remain in the cakes. If it be desired to obtain larger quantities of oils and fats than can be obtained by pressure, processes having for their object the extraction of the seeds by means of volatile solvents must be resorted to.

The solvents employed on a large scale are almost exclusively petroleum ether and carbon bisulphide; ordinary ether must be considered as altogether outside the range of the solvents used on a large scale owing to considerable loss of solvent involved, and, furthermore, on account of the great danger of fire. The same danger attaches, although in a somewhat minor degree, to the employment of petroleum ether. More diminished still is the danger of an inflagration in the case of carbon bisulphide; as this solvent is heavier than water, the vapours are less likely to come in contact with an open flame. Hence carbon bisulphide is largely employed for the extraction of oil, notably for the extraction of the marc of olives. Still, owing to the physiological effect this solvent has on the workmen, coupled with

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[1] With regard to the iodine value of oil extracted from linseed cake, cp. Ketel and Antusch; also Mastbaum, *Journ. Soc. Chem. Ind.* 1896, 150, 471.

[2] Emmerling, *Landw. Versuchs. Stat.* 1898, 56.

the danger caused by the action of impure carbon bisulphide on iron, which has frequently led to conflagrations, the employment of carbon bisulphide is restricted.

An ideal solvent would be carbon tetrachloride, which is non-inflammable, and has the further advantage of being heavier than water. Its high price has, however, hitherto prevented its technical application. Furthermore, its physiological effect (similar to that of chloroform) on the workmen would seem to prevent its general application.

The type of apparatus employed on a large scale depends on the temperature at which the extraction is carried out. In the case of cold extraction, preferable as regards fire insurance, the seed is placed in a series of closed vessels through which the solvent percolates on the counter-current system. The battery of vessels is so arranged that any one vessel can be made the last of the series, ready to discharge the extracted meal, and to be refilled with fresh meal, so that, with the exception of the time required for discharging and recharging, the process is a practically continuous one. The solution of extracted oil or fat in the solvent is then transferred to a steam heated still, where the solvent is driven off, and recovered by condensing the vapours in a cooling coil, to be used over and over again. The last traces of volatile solvents in the oil or fat are driven off by a current of open steam, which is blown through the oil or fat in the warm state.

The extracting processes in the hot are carried out in apparatus, the principle of which is illustrated by Fig. 59. (It should be noted that the condensing apparatus is not shown.)

The principle involved in more elaborate forms of apparatus employed on a large scale is exemplified by the *Soxhlet* extractor. The extraction thus takes place continuously, with a limited amount of solvent charged once for all into the apparatus. When the seed is deemed completely exhausted, the vessel containing the seed is disconnected by closing taps between the oil-containing vessel and the condenser, so that the volatile solvents can be immediately distilled off and condensed, whilst the seed-containing vessel is freed from last traces of volatile solvents by open steam and then emptied and recharged with fresh seed. More compact still are extractors illustrated by that form of laboratory apparatus in which the meal-containing vessel is placed inside the flask charged with the solvent. Thus in some form of extractors a basket containing the crushed seed is placed on a support at some height above the bottom of the vessel charged with the solvent, so that, on heating, the vapours of the solvent pass through and round the seed, whilst that portion which leaves the vessel in form of vapour is condensed in a separate condenser from which the liquefied solvent falls back and again percolates the seed in its liquefied state. Finally, when the meal is exhausted, the solvent is driven off, and the condensed solvent collected in a separate vessel.

Since apparatus of the type described here are illustrated in the catalogues and advertisements of engineering firms, no useful purpose can be served by a reproduction in this work.

As regards the merits and demerits of the two classes of processes described—expression and extraction—the adoption of either will largely depend on local factors and on the object for which the resulting products are intended.

It is obvious that extraction processes cannot be employed for the preparation of edible oils and fats, for however carefully the last traces of solvents may be removed, there is left sufficient to impart to the oil or fat a nauseous taste, rendering it entirely unfit for consumption.

Extracted oils and fats can, therefore, only be used for technical purposes.

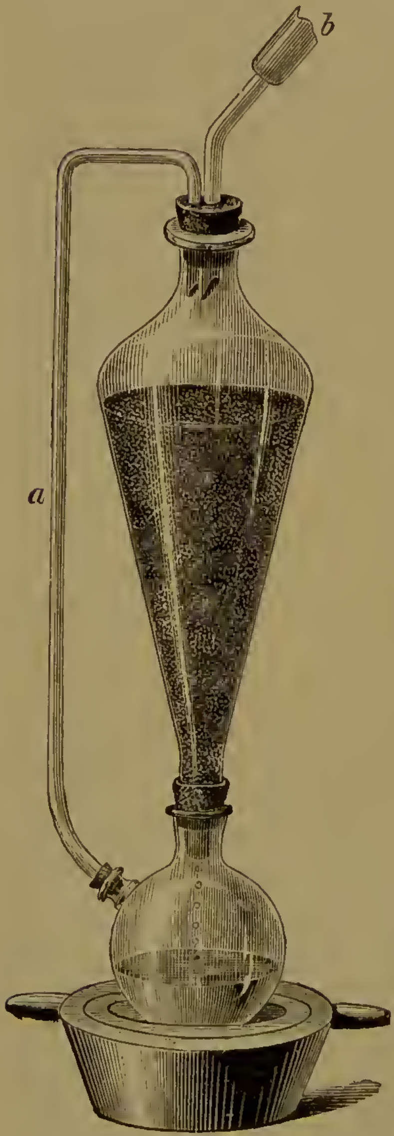

Fig. 59.

The extracted meal should also be considered as unfit for cattle feeding, notwithstanding the many statements of interested parties that the meal is fit for this purpose, and possesses even a greater value than expressed cakes on account of its higher proportion of albuminoids and carbohydrates when contrasted with press cakes. The oil or fat in an expressed cake has undoubtedly a certain value from a stock-raising point of view, whilst extracted meal to which is added so much oil or fat as to equal the proportion contained in the pressed cakes has not the same nourishing value. This holds good even if we leave out of account the contamination of the meal with the non-removable portion of the volatile solvent. On the Continent extracted meal, especially rape meal from good Indian seed and palm kernel meal, is being somewhat largely used as food for cattle, in admixture with press cakes (manufacture of compound cakes). Some outlet for extracted meal in this direction is stated to occur also in this country, but the bulk of the extracted meal finds its proper use in manuring the land.

Wherever the cake is the main product, the process of expression will commend itself as the more advantageous one. With regard to those fruits and seeds, however, the fatty material of which forms the main product, as in the case of palm kernel oil and cocoa nut oil, the economical factor militates to a much smaller degree against the extracting process, especially when it is possible to dispose of the extracted meal for feeding purposes.

In special cases, notably so in the manufacture of olive oils, a combination of the two processes commends itself. The combined method consists in expressing most of the oil for edible purposes, etc., and then extracting the partially expressed material with volatile solvents, in order to recover the oil left in the press cakes. This combined process is known on the Continent under the name "mixed process" ("huilerie mixte").

Animal oils and fats are usually obtained in a very simple manner by heating those parts of the animals which contain the oil or fat, so as to cause bursting of the fat-containing cells. The older rough and ready method of heating the adipose tissue of the animals over free fire may be considered as almost extinct in this country, but it is still being practised in small establishments on the continent. The nuisance which follows in the wake of a manufacturing process of this kind has naturally led to stringent regulations on the part of the sanitary authorities.

The rendering of tallow from the "rough fat" as it comes from the slaughter-house to the rendering establishment is nowadays carried out under such conditions that no serious objections can be raised from a sanitary point of view. The simplest, and, as I can testify from my own experience, a very effective method for obtaining tallow for technical purposes is to throw the rough fat into covered lead-lined vessels provided with steam coils, outlet taps, a trap-door for charging the rough fat, and a wide outlet through which any offensive vapours that may be given off are conducted through closed pipes to the chimney stack or fire grate. Hot water is then run on to the fat and steam turned on. After heating for a sufficient length of time the steam is shut off, when the clear melted fat rises to the top. It can then be drawn off ready for use or into another vessel for further purification (refining, bleaching). The animal tissue, etc., still containing considerable quantities of fat, is boiled up again with steam after a few per cent of dilute sulphuric acid have been added, whereby the cell membranes are "cut," so that they more readily part with the remainder of the occluded fat.

This second operation yields a somewhat inferior kind of fat as regards odour and colour; the proportion of free fatty acids is, however, not increased thereby, since dilute sulphuric acid is incapable of effecting hydrolysis.[1]

The foregoing method yields, for technical purposes, good raw material. Therefore processes (patented recently) involving the melting out *in vacuo* are an unnecessary complication of a simple operation.

Since, in the older method of melting the rough fat over free fire, not infrequently fat would burn on to the sides of the vessels, or

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[1] Cp. Lewkowitsch, *Journ. Soc. Chem. Ind.* 1903, p. 73; also chapter ii. p. 43.

even boil over and run into the flue, whereby volumes of acrolein were sent into the atmosphere, a number of apparatus have been designed in which the tallow is melted in closed vessels under pressure. Such vessels—termed digesters—consist essentially of a vertical boiler provided with a false perforated bottom, and constructed to withstand a pressure of several atmospheres. Live steam is turned into the boiler below the perforated bottom on which the rough fat rests; at the elevated temperature the mass parts readily with its occluded fat, and in a shorter time than by steaming at the ordinary pressure. An apparatus of this kind, designed by *Wilson*, is shown in Fig. 60; it has served as a prototype for a number of more or less complicated digesters now in use.

The rendering of lard in the large packing houses in the United States is carried out on similar lines. More primitive are the methods for obtaining blubber and liver oils. These methods, as also the rendering of animal oils and fats for edible purposes, will be described under the headings of the individual oils and fats in the following chapter, and in Chapter XV.

Refining and Bleaching

The oils and fats prepared by any of the methods detailed above are in their fresh state practically neutral. If care be exercised in the process of rendering animal oils and fats, the fatty matters are very often sufficiently pure to be immediately worked up in those industries to which they serve as raw materials.

The vegetable oils obtained by expression contain frequently mucilaginous matter and other impurities, such as vegetable fibres, which pass through the press cloths. There are also admixed with the oils traces of moisture, which render them somewhat turbid. Formerly these impurities were removed by the simple method of allowing the oils to rest for some prolonged time, when the moisture and the mucilaginous matter, etc., would settle out. This crude process is no longer employed in large establishments, the process of clarifying being much shortened by filtering the oils through a filter press, or brightening them by blowing with air. In many cases these methods suffice for the production of commercial oils and fats. In special cases the filtration is combined with purification by filtering the oils over charcoal or fuller's earth, as is done in the case of edible oils (cp. chap. xv.).

In other cases the crude oils require further purification or refining before they can be placed on the market as raw material. Notable examples of this kind are rape oil and cotton seed oil. The processes adopted on a manufacturing scale vary greatly with the nature of each individual oil or fat. It will therefore be most convenient to consider the refining and purifying under the heading of each individual oil or fat.

The methods of bleaching or decolourising also vary with each kind of oil or fat, hence it must suffice here to very briefly glance at the methods employed on a large scale.

Bleaching by means of *charcoal* is naturally the most expensive process, and it can therefore only be applied to the most valuable materials, such as edible oils and fats.

Bleaching in *sunlight* is commercially feasible on a small scale only, as the length of time and the space required to expose as large as possible a surface must naturally be costly. Still, in some cases, as in the bleaching of beeswax, or in the bleaching of linseed oil for artists' use, this method is being practised. Since the fatty matter undergoes practically no change, the products do not suffer as much as they do in chemical processes.

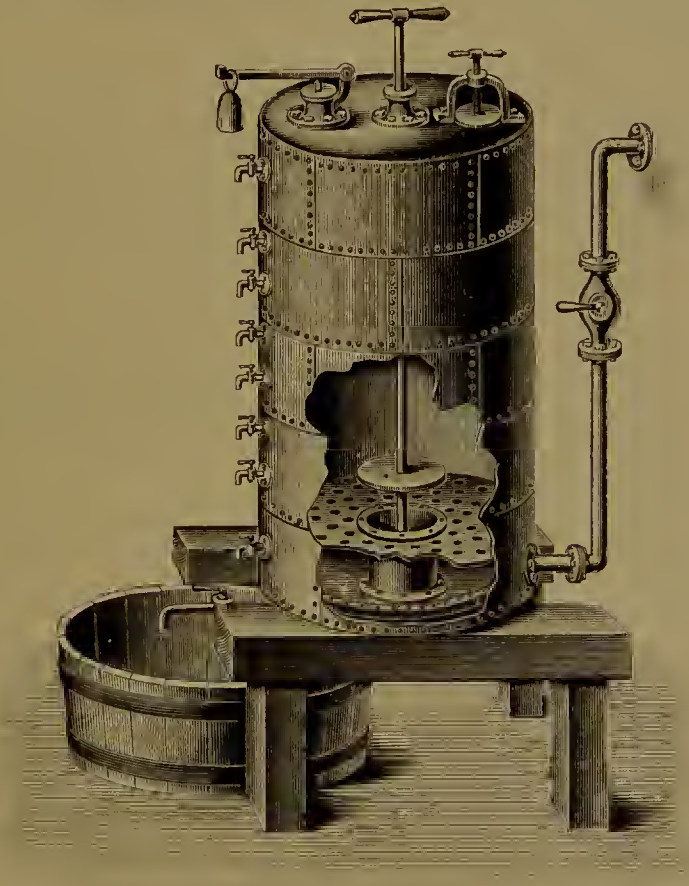

Fig. 60.

Bleaching by the aid of *chemicals* requires great circumspection, the object of bleaching being merely to destroy foreign substances, which impart a dark colour, or other undesirable properties, to the oil or fat. The chief attention of the operator must therefore be directed to so treating the raw material that the fatty matter itself is not acted upon. For this purpose the amount of chemicals must be limited to the smallest possible quantity, the temperature at which they are allowed to act must be as low as possible, and the time of interaction must be as short as possible.

General methods of bleaching, the applications of which will be described under the headings of those individual oils and fats for which they are most suitable are: (1) bleaching by means of oxygen; (2) bleaching by means of chlorine.

(1) Bleaching by means of ozone or oxygen gas is still too uncertain a process to be widely used on a large scale, although it is practised in some special instances. Bleaching by oxygen in *statu nascendi* is chiefly effected by employing manganese dioxide or potassium bichromate and sulphuric acid.

The chemical reactions involved are expressed by the following two equations:—

$$(1)\ MnO_2 + SO_4H_2 = SO_4Mn + H_2O + O$$
$$(2)\ Cr_2O_7K_2 + 4SO_4H_2 = (SO_4)_3Cr_2 + SO_4K_2 + 4H_2O + 3O.$$

In the processes of bleaching by means of chlorine, bleaching powder, or potassium bichromate and hydrochloric acid are used. The following two equations represent the chemical reactions:—

$$(3)\ Ca(ClO)_2 + 4HCl = CaCl_2 + 2H_2O + 4Cl$$
$$(4)\ Cr_2O_7K_2 + 14HCl = Cr_2Cl_6 + 2KCl + 7H_2O + 6Cl.$$

No general rule can be laid down as to which process should be employed in each given case, although it may be stated that tallow is best bleached by means of manganese dioxide, and palm oil by means of bichromate and hydrochloric acid.

The object of bleaching is not only to remove colouring matters for the time being, but to remove them so efficiently that the colour, or even a dark shade, does not "revert" some time after the fat or oil has been bleached. Patents claiming to effect this object appear annually in great numbers, and disappear again when experience has shown that the colouring matter does "revert," to a larger or smaller extent, after the material has, *e.g.*, been converted into soap. Thus one of the simplest and most frequently practised processes, that of bleaching tallow, does not produce soaps as good in colour as those made from the freshly rendered tallow. Not only must each kind of fat or oil be considered a special problem, but frequently different varieties of one and the same fat or oil are apt to cause the same difficulties as would a new individual. To mention an example, the bleaching of the softer kinds of palm oil, such as "Lagos" or "Old Calabar," offers very little difficulty. But the hardest kinds of palm oil, such as "Congo" oil, have hitherto withstood all attempts to bleach them.

There is therefore still great scope for the application of proper processes, but their number must be naturally limited for the reasons stated above, namely, that the glycerides themselves are too easily attacked.

The separation of solid glycerides from liquid glycerides—"demargarinating processes"—will be mentioned under the heading of those products which are resolved on a commercial scale into a liquid and solid portion.

Processes for extracting animal fats by means of volatile solvents are only employed in the solitary case of bone fat.

The preparation of waxes has not yet reached the dimensions of a manufacturing process, and is hardly likely to attain that position Even in the case of beeswax, simple machinery has only been introduced lately. The preparation of vegetable waxes must remain an industry in which hand labour is almost exclusively employed.

CHAPTER XIV

DESCRIPTION OF THE NATURAL OILS, FATS, AND WAXES; METHODS OF PREPARING AND EXAMINING THEM, AND DETECTING ADULTERATIONS

In this chapter the individual oils, fats, and waxes are arranged according to the classification outlined in Chapter I. In the first instance, the mode of preparation and refining, wherever this is carried out on the large scale, will be considered; next the chemical composition will be given, as far as it is known. I append in each case tables of the physical and chemical characteristics, as recorded by various observers, and I further add the variations — within narrow limits—of these constants, as found in the examination of different specimens of the same kind, wherever these variations are due to difference of source, climate, soil, mode of preparation, race or breed of animal, mode of feeding, and, finally, age of the sample. Thus this chapter gives in a handy form that information which is obtained by applying the methods described in Chapters V.-XI.

It is hoped that by first scanning the tables the analyst will have placed before him a ready means of identifying any unknown oil or fat which he may have to examine. In each case a discussion of those factors will follow which influence the chemical composition. Next those adulterants will be considered that are most likely to be met with. Methods of testing for adulteration and determining its amount will also be fully described. It should be mentioned that I have examined in the course of many years most of the products described below; especially those that are of great commercial importance. I did not consider it necessary to record my name in each case amongst the observers, but it should be pointed out that the colour reactions to which, in former years, so much importance has been assigned, have been especially examined by me. In the course of these investigations most of the colour tests have been found useless; these have been therefore omitted in this treatise.

The order in which the oils, fats, and waxes are enumerated in the subsections is determined by the magnitude of the iodine value. I have frequently ascertained the iodine values merely for the sake of fixing the order which individual oils or fats should follow. I have, however, not considered it advisable to slavishly follow this principle; hence such oils and fats as are undoubtedly related to one another are placed together irrespective of differences in their iodine values.

It should further be pointed out that I have carefully scrutinised the numerical values given in the tables. Older numbers which are obviously wrong, or have been obtained by incorrect methods, have been omitted, and only the most reliable numbers have been tabulated. The French, German, and also Italian names have been added, wherever ascertainable.

A. OILS AND FATS. GLYCERIDES

I. OILS OR LIQUID FATS

1. VEGETABLE OILS

(1) Drying Oils

The drying oils are characterised by their property of absorbing oxygen from the atmosphere, and drying to an elastic skin. It has been pointed out already that the drying power stands in direct proportion to the magnitude of the iodine value, so that the best drying oils are those which absorb the greatest amount of iodine.

Considered chemically, they are characterised by the presence of acids belonging to the linolenic and linolic groups, the glycerides of oleic acid forming only a small proportion of the liquid fatty acids. Hence the drying oils do not give the elaïdin reaction. Glycerides of saturated acids are present in small proportions only.

As regards the drying power, there is a slow gradation from the best drying oils down to those standing at the end of the class. The properties of the last-named oils approach more or less those of the semi-drying oils. In the best drying oils, linolenic acid forms a considerable proportion of the liquid fatty acids. The readiest means of ascertaining the amount of the linolenic acids is afforded by the hexabromide test.

PERILLA OIL

French—*Huile de perilla.* German—*Perillaoel.*

Perilla oil occurs to an extent of 35·8 per cent in the nuts of *Perilla ocymoides*, a plant indigenous to the East Indies, as also to China (Manchuria), and Japan. The seed is known in Japan as Ye-Goma, or Se-no-abura.

This oil has the highest iodine value of any known fatty oil, and simulates linseed oil in taste and smell. Contrary to expectation, its drying power is inferior to that of linseed oil, although it absorbs up to 20·9 per cent of oxygen. The inferiority in drying may be due to the curious property of the oil of forming drops (like mercury) when spread on a surface.

The specimen examined by *Wijs*[1] contained 0·48 per cent free fatty acids; it gave no colour reaction in the *Halphen* and *Baudouin* tests.

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[1] *Zeit. f. Nahrungs- und Genussm.* 1903, 492.

Physical and Chemical Constants of Perilla Oil

Specific Gravity.	Saponification Value.	Iodine Value.
At 20° C. (Water 20° = 1.)	Mgrms. KOH.	Per cent.
0·9306	189·6	206·1

Physical and Chemical Constants of the Mixed Fatty Acids

Melting Point.	Neutralisation Value.	Mean Molecular Weight.	Iodine Value.
°C.	Mgrms. KOH.		Per cent.
− 5	197·7	284·0	210·6

The perilla plant is cultivated in the Himalayas and in Manchuria,[1] and the oil is used for edible purposes. In Japan the oil is employed in the manufacture of varnishes and in the extraction of the last quantities of Japan wax from the berries by mixing the press residues with 10 per cent of perilla oil.

LINSEED OIL, FLAX SEED OIL

French—*Huile de lin.* German—*Leinoel.* Italian—*Olio di lino.*

For tables of constants see pp. 450-452.

Linseed oil is obtained from the seeds of the flax plant, *Linum usitatissimum*, L. The principal countries where it is grown in considerable quantities to yield oil seeds are Russia, India, the United States, Canada, and Argentina. Two qualities of Russian seed are recognised in the trade, and known, according to their source, as Baltic and Black Sea seed; hence the terms "Baltic linseed oil" and "Black Sea linseed oil." The oil expressed from Indian seed is known as East India oil. The Baltic linseed yields the best drying oil; this is explained by the fact that the Baltic seed is the purest, whereas in Black Sea seed 5 per cent (and more) of hemp seed or ravison seed are usually present, and Indian seed is always mixed with mustard, rape, and cameline seed, owing to the plants yielding the latter being grown along with the flax plant. It has been proved that when the Indian linseed was carefully separated from the foreign seeds and then expressed, the oil

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[1] A. Hosie, Manchuria, Methuen and Co., 1901.

Physical and Chemical Constants of Linseed Oil

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ Norm. KOH.	Observer.
12	0·939	Saussure	−27	Chateau	−16 to −20	Glaessner	190·2-192·7	De Negri and Fabris	173·5-187·7	Thomson and Ballantyne	0·00	Crossley and Le Sueur[2]
15	0·932-0·937	Allen	at −25 "stearine" deposits	Lewkowitsch			195·2	Moore	173-193	Lewkowitsch		
,,	0·9315-0·9345	Thomson and Ballantyne					190-192	Thoerner	183-188	Williams		
,,	0·9342	De Negri and Fabris					192·2-195·2	Lewkowitsch	160-180[3]	Gill and Lamb		
15·5 (water at 15·5 = 1)	0·9316-0·9410	Lewkowitsch[1]					191·5	Crossley and Le Sueur[2]	176·3-201·8	Wijs[4]		
,,	0·931-0·938	Gill and Lamb[3]										
,,	0·9337	Crossley and Le Sueur[2]										
18	0·9299	Stillwell										
25	0·930	Saussure										
50	0·921	,,										
94	0·881	,,										
99 (water at 15·5 = 1)	0·8809	Allen										

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[1] Cp. table, p. 457.

[2] East Indian oil from the Central Provinces.

[3] North American oils (*Journ. Soc. Chem. Ind.* 1899, 282).

[4] Cp. table, p. 459.

Physical and Chemical Constants of Linseed Oil—continued

Helmer Value.		Thermal Tests.				Refractive Index.			Viscosity.	
		Maumené Test.		Heat of Bromination.						
Per cent.	Observer.	°C.	Observer.	°C.	Observer.	At °C.		Observer.	Seconds at 70° F.	Observer.
94·81	Crossley and Le Sueur[4]	103	Maumené	30·4-31·3	Helmer and Mitchell	15	1·4835	Strohmer	211·7	Crossley and Le Sueur[4]
						60	1·4660	Thoerner		
95·5 (mean value)	Lewkowitsch			31·4-32·5[1,2]	Archbutt					
		104-111	Allen	29·8-30·5[1,3]	,,		Oleo-refractometer.			
		122-126	De Negri and Fabris	30-33	Bromwell and Meyer[6]		"Degrees."	Observer.		
		90-106[5]	Gill and Lamb				+48 to +53	Jean		
		128-145	Archbutt				+48 to +52	Bruyn and van Leent		
		Specific Temperature Reaction.				22	+50 to +54	Permain		
		320 to 349	Thomson and Ballantyne			Butyro-refractometer.				
		313	Jenkins			At °C.	"Degrees."	Observer.		
						20	84-90	Lewkowitsch[7]		
						25	81-87	,,		
						40	74·5	White[8]		
						,,	72·5	Crossley and Le Sueur[4]		

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[1] The rise of temperature observed multiplied by two, as 0·5 grm. of oil only was used.
[2] Baltic oil.
[3] East India oil.
[4] East India oil from the Central Provinces.
[5] North American oils.
[6] *Amer. Journ. Pharm.* 1897, 145.
[7] Six oils described, *Chem. Revue*, 1898, 211.
[8] *Journ. Soc. Chem. Ind.* 1900, 1089.

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.			Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.		Refractive Index.		Hexabromides.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.	At 60° C.	Observer.	Per cent.	Observer.
15·5	0·9233	Allen	13·3	Hübl	17	Hübl	198·8	Dieterich	283	Williams	178·5	Williams	1·4546	Thoerner	18-23	Hehner and Mitchell
99 (water at 15·5 = 1)	0·8612	,,	17·5	Allen	24	Allen	196	Thoerner			179-209·8	Lewkowitsch			29·1-31·3	Walker and Warburton
			13·5	Thoerner	Below 13	Dieterich									30-41·9	Lewkowitsch[4]
100 (water at 100 = 1)	0·8925	Archbutt	16-17	De Negri and Fabris	20-21	De Negri and Fabris					Liquid Fatty Acids.				—	
			Titer Test.								201·4	Tortelli and Ruggeri[1]			Liquid Fatty Acids.	
											190·1-193	,, [2]				
			19·0-19·4	Lewkowitsch							208-209·8	Lewkowitsch[3]			34·9	Walker and Warburton
			20·2-20·6	,,												

[1] Cold pressed oil, of iodine value 179·4.

[2] Italian oils, 1898 and 1899 crop, of iodine values 173·4-176·8.

[3] East Indian oil, iodine value 184.

[4] Unpublished results.

possessed as good drying properties as best Russian oil. During latter years, more attention having been paid in India to this growing industry, the quality of seed has improved. South American seed, yielding the River Plate oil, is largely imported into this country, but being badly harvested it contains much chaff and admixed fibres; if more care were exercised, La Plata oil also would approach Baltic oil in drying properties. Canadian seed is imported in smaller quantities than from the above-mentioned countries. The United States are still importing East Indian seed, although the home production has increased considerably.

Linseed arriving in this country is sampled and tested by the Linseed Association, who ascertain the proportions of linseed and foreign seeds; oil-yielding seeds other than linseed are reported as having half the value of the latter, whereas non-oleaginous seeds are considered as valueless.

The proportion of linseed oil in the seed varies with the origin of the seed, and also with the seasons. The figures given below should, therefore, only be considered as average numbers. It should also be remembered that on extracting seeds with ether larger quantities of crude oil are obtained than on extracting with petroleum ether.

	Per cent.
Russian linseed yields oil . . .	32-38
Indian ,, ,, ,, . . .	37-41
River Plate ,, ,, ,, . . .	35-36

On cold pressing, a golden-yellow coloured oil is obtained, having a pleasant taste, so that it can be used as an edible oil. Considerable quantities are being expressed for this purpose in Russia, Hungary, and India. By far the largest quantities of oil are, however, prepared for industrial purposes (see below). The seed is crushed between rollers and then heated up to about 160° F. in the mixing kettle; subsequently the seed is expressed whilst still warm. The oil so obtained has a yellowish brown hue and is somewhat turbid, due to traces of moisture and mucilaginous matter. The press cakes retain about 10 per cent of oil.

On storing the oil, the moisture and the mucilaginous matter gradually settle out, and the oil thereby acquires a higher value, especially for some technical uses, as in the making of varnish. Such oil, sometimes kept for years, is known as "tanked oil." The usual test for suitability for varnish-making purposes is to heat the linseed oil in a test-tube. Oil which separates gelatinous matter is considered unsuitable. Seed pressed in a comparatively fresh ("green") state yields oil containing larger quantities of "mucilage" than seed, three to six months old. The gelatinous matter, "mucilage" or "spawn" or "break," consists of phosphates and traces of sulphates. *G. W. Thompson*[1] found that a sample of freshly expressed linseed oil heated to 400° F. yielded 0·277 per cent of a precipitate. On

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[1] *Journ. Soc. Chem. Ind.* 1903, 1005.

washing it with petroleum ether to remove the oil completely, this foreign substance gave 47·79 per cent of ash (0·1177 per cent of the original oil), consisting of 20·96 per cent calcium oxide, 18·54 per cent magnesium oxide, 59·85 per cent phosphorus pentoxide, and traces of sulphate. Other samples of linseed oil gave the following results :—

Description.	Ash. Per cent.
1. Fresh double-filtered raw American linseed oil .	0·1429
2. ,, ,, ,, .	0·1967
3. Good well-settled ,, ,, .	0·0609
4. Best American linseed varnish oil . . .	Traces

As mentioned already, the impurities settle out on long standing, and the enhanced value of "tanked oil" consists in the comparative freedom of such oil from foreign substances. A more rapid method of removing these impurities is to refine the oil. This is indeed done on a large scale for better-class linseed oil, such as paint oils. The process consists in treating linseed oil with 1 to 2 per cent of a somewhat concentrated sulphuric acid. The charred mass carries down with it the bulk of impurities contained in the crude oil. For the manufacture of the best and finest kinds of linseed oil (artists' oil), the refined oil is subjected to "sun-bleaching," by exposing the oil in shallow trays under glass to the action of sunlight.

A number of patents have been taken out for the refining of linseed oil by means of ozone; the writer has examined several processes worked on a semi-large scale, but none of them can be said to have superseded the usual methods.—Attempts made by the writer to remove the solid glycerides from linseed oil on a commercial scale, with a view to obtaining an oil of still higher drying power than is possessed by refined oils, have not proved successful. The value of the method patented by *Hertkorn*[1] for achieving the same object appears therefore rather doubtful.

The chemical composition of linseed oil is but imperfectly known. According to *Mulder* the oil contains about 10 per cent of glycerides of solid fatty acids, consisting of palmitic and myristic acids in about equal proportions. The solid acids separated off by means of the lead-salt-ether method contained, however, notable quantities of liquid acids. *Tolman* and *Munson*[2] found by the same method 3·88 per cent of solid acids only. The liquid glycerides consist, according to *Hazura* and *Grüssner*, of 5 per cent oleic acid, 15 per cent linolic acid, 15 per cent linolenic acid, and 65 per cent isolinolenic acid. On calculating the theoretical iodine value of the mixed fatty acids from the composition of the liquid acids as stated, and allowing as a *maximum* 10 per cent of solid acids, a much higher iodine value should result than is ascertainable by experiments. This is shown by the

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[1] German patents 129809 and 137306; cp. *Jahrbuch der Chemie*, xii. 370.

[2] *Journ. Amer. Chem. Soc.* 1903, 960.

following calculation. A mixture of fatty acids having the following composition

	Per cent.
Solid acids	10
Oleic acid	4·5
Linolic acid	13·5
Linolenic acid	13·5
Isolinolenic acid	58·5
	100·0

should absorb, theoretically, 225·89 per cent of iodine. The liquid fatty acids, freed from solid acids, should therefore have the calculated iodine value of 250·9, whereas the highest number found in my laboratory for the liquid fatty acids (prepared by *Tortelli* and *Ruggeri's* method) was only 210. To explain the discrepancy *Fahrion* assumed that raw linseed oil is polymerised during the process of manufacture. This assumption, however, cannot be substantiated.

More recently *Fahrion*,[1] basing himself on a casual remark in a paper by *Hazura*, that isolinolenic hexabromide is very likely soluble in ether, assumes the following composition of linseed oil :—

Unsaponifiable	0·8	per cent.
Palmitic and myristic acids	8·0	,,
Oleic acid	17·5	,,
Linolic acid	26·0	,,
Linolenic acid	10·0	,,
Isolinolenic acid	33·5	,,
C_3H_2	4·2	,,
	100·0	

Since, however, higher amounts of linolenic hexabromide have been found than correspond to 10 per cent of linolenic acid, the above composition can hardly be accepted, all the less so as the amount of oleic acid is far higher than can possibly be present in linseed oil. The assumptions underlying the above composition must therefore be accepted with the greatest reserve. More acceptable is *Fokin's*[2] statement that linolic acid predominates amongst the liquid fatty acids, linolenic acid only constituting 22-25 per cent of the mixed fatty acids. This figure is in much better agreement with the yield of hexabromides from the mixed linseed oil fatty acids, as obtained in my laboratory, although *Fokin's* statement that the solid fatty acids form 5 per cent only is not in agreement with *Mulder's*, *Fahrion's*, and my own results. From the percentage of hexabromide, 42 per cent, I found (see table) the calculated proportion of linolenic and isolinolenic acids (assuming that *both* acids yield an ether-insoluble hexabromide) is 15·4 per cent only, since 100 parts of hexabromides correspond to 36·68 parts of linolenic acids. This amount may be below the true one; but the deficiency is not sufficiently

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[1] *Zeit. f. angew. Chem.* 1903, 1193.

[2] *Journ. Chem. Soc.* 1902, Abstract I. p. 740 ; *Journ. Russ. Phys. Chem. Soc.* 1902, 501.

explained by assuming that some hexabromide was dissolved out together with linolic tetrabromide, for experiments which I have made with varying amounts of bromine and ether did not lead to results differing materially from the above-named percentage of hexabromide, viz. 42 per cent. The following is an example of an examination of linseed oil carried out in my laboratory :—The sample had the iodine value 190·4 ; it yielded 37·72 per cent of hexabrominated glycerides and 8·9 per cent of solid acids of the iodine value 22·3 (by the lead-salt-ether method). After passing the solid acids once more through the same process, 7·5 per cent of solid fatty acids of the iodine value 19·2 were obtained. The mixed fatty acids had the iodine value 194·4, and yielded 38·1 per cent of hexabromide of the melting point 176·4° C. Attempts to obtain further quantities of hexabromides from the ethereal filtrate failed. The amount of hexabromides found leads to 14 per cent of linolenic and isolinolenic acids. But even on the assumption that linseed oil contains no oleic acid—the dihydroxystearic acid obtained by *Hazura* being a product of secondary reaction—the iodine value of the mixed fatty acids would only work out at 182·2, as shown by the following calculation :—

	Per cent.	Iodine Value.
Solid fatty acids of the iodine value 19·2	7·5	1·4
Linolenic and isolinolenic acids . .	14·0	38·4
Linolic acid, by difference . . .	78·5	142·4
		182·2

whereas the experiments led to 194·4.

It is evident that further researches are required to satisfactorily establish the composition of the linseed oil fatty acids.[1]

On exposure to air linseed oil readily absorbs oxygen, and when spread in a thin film on a large surface it dries to a neutral substance, insoluble in ether. This substance, the nature of which has not been ascertained hitherto, is termed "linoxyn," and is in its turn further oxidised to a liquid substance—superoxidised oil (cp. chap. xv.).

The ready absorption of oxygen may explain the occurrence of small amounts of "oxidised" acids in even comparatively fresh oils. When kept protected from moisture, air, and light, linseed oil keeps indefinitely, as shown in the following table, which contains the proportions of "oxidised" acids in some (comparatively) fresh and old linseed oils examined by *Lewkowitsch*[2] (together with a few other "constants" and "variables") :—

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[1] Cp. also p. 126 (Reformatzky).

[2] *Journ. Soc. Chem. Ind.* 1899, 51 ; *Chem. Revue*, 1898, 211.

	"Oxidised" Acids. Per cent.	Specific Gravity. At 15·5° C. (water 15·5=1).	Butyro-refractometer. "Degrees." At 20° C.	At 25° C.	Saponific. Value.	Iodine Value.	Acid Value.	Unsaponifiable. Per cent.
Oil from finest Calcutta seed, 2 months old	0·65	0·9316	84	82	193·2	170·46	1·3	0·65
Oil from finest Calcutta seed, 3 years old, kept the whole time protected from air and light	0·7	0·9324	84	81	192·5	174·0	1·3	0·7
Finest St. Petersburg seed, 3 months old	0·88	0·9334	86·5	84	192·2	177·3	1·3	1·1
Finest St. Petersburg seed, 7 months old	0·56	0·9345	87	84	193·1	176·2	1·3	0·98
Baltic (commercial) seed, containing ravison and cameline seed	0·73	0·9343	86·5	84	194·3	170·1	1·3	1·1
Finest and purest Baltic seed, kept 13 years protected from air and light	1·95	0·9410	90	87	195·2	175·8	7·2	1·1

As will be gathered from the preceding table, the proportion of free fatty acids in linseed oil is as a rule small; it rarely exceeds in good commercial samples 1-1·5 per cent. The acetyl value of linseed oil was found by *Lewkowitsch* 3·9. The proportion of unsaponifiable matter varies in commercial samples from 0·3 to 1·2 to even 2 per cent (in River Plate oil), the amount depending on the care with which the manufacture has been carried out.[1]

The following tests will serve for the identification of a sample.

Specific Gravity.—Linseed oil has a higher specific gravity than any fatty oil that would be used to adulterate it, with the exception of tung oil. Hence a lower specific gravity than 0·93 in a given sample would direct attention to the presence of other fatty oils or mineral oils. A higher gravity would indicate probable adulteration with rosin oils. "Boiled linseed oil" has a higher specific gravity than linseed oil; its presence would in the first instance be detected by the specific gravity test.

The higher the specific gravity of a linseed oil, the more suitable it is for the purposes of the paint and varnish manufacturer. This is also expressed in a general way by the magnitude of the iodine values. Thus *Wijs*[2] has shown that the specific gravities of a number of linseed oils varied from 0·9310 to 0·9352 as their iodine values varied from 180·1 to 200. On storing, "tanking," the specific gravity increases, as shown by the numbers recorded in the last given table.

The increase must be ascribed to a slight oxidation of the oil, due to the absorption of oxygen, and not to polymerisation.

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[1] A number of determinations of the unsaponifiable matter in linseed oils of different origin has been carried out recently by Niegemann (*Chem. Zeit.* 1904, 97). The percentages varied from 0·83 to 2·1 per cent.

[2] *Chem. Revue*, 1899, 29; *Journ. Soc. Chem. Ind.* 1899, 591.

Iodine Value.—Linseed oil has, with the exception of perilla oil, the highest iodine value of all known fatty oils. Hence the iodine test is the most characteristic test to be used for identifying a sample. The iodine numbers given by earlier observers are much too low, owing to too small an excess of iodine solution having been used. These incorrect values have therefore not been recorded in the above given tables. Correct iodine values are obtained by allowing the *Hübl* iodine solution to act 18 hours; on using the *Wijs* iodine solution one to two hours are sufficient. In either case an excess of iodine must be present, about equal to the quantity of iodine absorbed.

If the iodine value of a sample falls below 170, the presumption that the sample has been adulterated is justified.

The adulteration may have taken place in the seed itself as it were, the oil having been produced from impure or adulterated linseed (see below).

Somewhat lower values than those given in the table may also be due to an oil having been exposed to the atmosphere, and thereby having absorbed oxygen. This point must be borne in mind before a sample can be pronounced adulterated, as purity of an exposed oil is quite consistent with a somewhat lower iodine value.

A high iodine value of itself is, however, not proof of purity, since fish oils, rosin oils, and even drying oils may be readily admixed with linseed oil in considerable quantities, and yet furnish numbers lying in the neighbourhood of those given in the table of constants.

The following table containing the iodine values of linseed oils from specified sources will be found useful :—

Kind of Linseed.	Iodine Value of Oil.	Observer.
Baltic	187·7	Thomson and Ballantyne
,, (cp. table, p. 475)	170-177·3	Lewkowitsch
Archangel, Wiatka, Petersburg, Reval, Pernau, Riga, Libau	188·5-200	Wijs
Central Russia (Samara, Steppes)	188·9-189·1	,,
Black Sea, Asoff; Taganrog	176·3-182·5	,,
East India	178·8	Thomson and Ballantyne
East India	170·5-174	Lewkowitsch
,,	182·2-187·5	Wijs
River Plate	173·5-175·5	Thomson and Ballantyne
,,	174·7-182·7	Wijs
,,	179-189	Lewkowitsch
Dutch	191·5-201·8	Wijs
North America	178·1-188·5	,,
,, ,,	160·0-178·8	Gill and Lamb
Danube countries	182·1	Wijs
Mixed; from—		
Dutch and Baltic	199·1	Wijs
Various Baltic seeds	198·4	,,
$\frac{2}{3}$ Baltic and $\frac{1}{3}$ Dutch	195·7-197·5	,,
$\frac{1}{2}$,, and $\frac{1}{2}$,,	195·1-195·4	,,
$\frac{2}{3}$ Black Sea and $\frac{1}{3}$ Baltic	185·5	,,
$\frac{1}{10}$,, and $\frac{9}{10}$ River Plate	183·7	,,
$\frac{1}{2}$ Black Sea, $\frac{1}{4}$ River Plate, $\frac{1}{8}$ East India, $\frac{1}{8}$ North America	183·3	,,
$\frac{1}{2}$ La Plata, $\frac{1}{3}$ East India, $\frac{1}{6}$ Black Sea	183·2	,,
$\frac{1}{8}$,, $\frac{3}{8}$,, $\frac{1}{2}$,,	182·9	
$\frac{2}{3}$ East India, $\frac{1}{3}$ Black Sea	182·7	,,
Black Sea and East India	181·5	,,
Black Sea, and East India, and North America	181·1	,,
$\frac{1}{2}$ Black Sea and $\frac{1}{2}$ East India	180·9	,,
$\frac{2}{3}$ River Plate and $\frac{1}{3}$ East India	180·1	,,
River Plate, Black Sea, East India	178·7	,,

Hexabromide Test.—This is an important test for purity. Pure linseed oils yield up to 38 per cent crude hexabrominated glycerides. From the table given in Chapter VII., p. 314, it will be noticed that all other drying oils can be readily differentiated from linseed oil by the hexabromide test, since tung oil, poppy seed oil, safflower seed oil, candle nut oil, either yield no hexabrominated glycerides or much smaller quantities only. If the yield of hexabrominated glycerides fall below 20 per cent, the presence of other oils than linseed oil may be inferred with certainty. I prefer to brominate the mixed fatty acids (prepared with due precaution against oxidation), as the linolenic hexabromide is easy to obtain in a comparatively pure state, which is readily ascertained by its melting point. Linseed oil mixed fatty acids yield from 30-42 per cent of hexabromide melting from 175°-180° C., whereas all other drying (vegetable) oils give much smaller quantities (cp. chap. viii. p. 365).

Since fish, liver, and blubber oils also yield high percentages of an insoluble bromo-product in the hexabromide test, the determination of the melting point of the hexabromides must not be omitted. Linolenic hexabromides from drying oils melt at 175°-180° C. to a *clear liquid*, whereas the hexabromides of fish, liver, and blubber oils do not melt at these temperatures, but become darker and are converted at about 200° C. into a black mass. Experiments carried out in my laboratory proved that it is thus possible to detect admixtures of 10 per cent of fish oil with linseed oil.

The **thermal reactions** which linseed oil gives are not characteristic enough for purposes of identification, and on account of their indefiniteness and the trouble involved in the determination, their employment is not recommended for isolated tests in an analytical laboratory. For special purposes, however, as in a works where a large number of tests must be made rapidly, the *Maumené* reaction, or, better still, the bromine thermal test, may be usefully applied.

Thus oils that are otherwise pure will be quickly sorted into those which have the lowest iodine value, and hence are suitable for soap-making purposes, and oils of a high iodine value which are preferably used in the manufacture of varnish and linoleum. It should, however, be understood that each operator must determine the factor which applies to the particular conditions under which the test is carried out. The following table will show how necessary it is for each operator to ascertain the factor which represents, as it were, the personal equation of his experiments.

Kind of Linseed Oil.	Bromine Thermal Value. °C.	Hübl Iodine Value. I.	I×5·5.	I×5·7.	I×6·0.	Observer.
..	30·4	160·7	167·2	...	...	Hehner & Mitchell
...	31·3	154·9	172·0	...	...	,, ..
Raw linseed .	30·55	174·3	...	173·9		Jenkins[1]
Old sample .	28·5	167·1	...	...	171·0	..
...	28·8	177·0	...	...	172·8	Archbutt[2]
American (?) .	29·6	177·0	...	...	177·6	..
...	29·7	177·8	...	...	178·2	..
East Indian .	29·8	178·7	...	...	178·8	..
.. .. .	30·45	183·3	...	...	182·7	..
Baltic . .	31·35	188·5	...	...	188·1	..
.. . .	31·4	188·8	...	...	188·4	..
.. . .	31·75	188·8	...	...	190·5	..
.. .	32·5	192·5	..		195·0	..

In doubtful cases the determination of the iodine value must of course be resorted to, as this only furnishes unmistakable results.

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[1] *Journ. Soc. Chem. Ind.* 1897, 194.

[2] *Ibid.* 1897, 311.

Oxygen Absorption.—The rapidity with which a given sample of linseed oil dries, and the amount of oxygen it absorbs, afford guidance in the valuation of an otherwise pure linseed oil. The commercial value of a sample of linseed oil intended for the manufacture of varnish depends on its drying power, which is determined by the amount of oxygen it absorbs, and also by the time it requires for drying to an elastic skin. The *Livache* method, as also the glass-plate method, may be applied for quantitative purposes, but except in special cases, little information can be derived therefrom. Of far greater importance is to observe the time required to dry, and the nature of the skin formed. This test is the one usually applied in technical work. It requires, however, a good deal of practical experience to judge of the quality of an oil by the drying test. The analyst who may be called upon to give an opinion, should compare a given sample with an oil of known composition as regards purity and quality by exposing side by side a number of glass plates coated with a very thin film of oil, by means of a palette knife, so that exactly the same conditions may obtain. A good linseed oil should become dry in less than three days; it should not be tacky on touching it with the fingers, and should yield an elastic coherent skin. Oils containing considerable amounts of unsaponifiable matter or foreign oils will be incidentally detected by this test, inasmuch as they prevent the formation of a good elastic skin.

An important test for judging of the suitability of a linseed oil for making paint oils and varnishes is to heat a few c.c. in a test-tube up to 600° F., that is, until the oil commences to boil up. Good oil should remain clear on cooling (as a rule it will have become lighter in colour). From impure oils mucilaginous matter will separate as a gelatinous mass at the bottom of the test-tube; in the case of low quality oils this mass will be found disseminated through the oil. Oils of this kind are unsuitable for the manufacture of paint and varnish oils.

Linseed Oil Soap Stock.—Incompletely saponified linseed oil, consisting of a mixture of linseed oil and linseed fatty acids, is now somewhat frequently found in the market. The proportion of the constituents is ascertained by determining the acid value of the sample.

Linseed oil, being one of the cheapest fatty oils, is not frequently adulterated with vegetable oils. However, when the price of linseed oil is high, other cheap drying oils, such as safflower oil and candle nut oil, may be employed as adulterants.

Drying Oils.—The presence of considerable quantities of drying oils is indicated by the iodine value being below 175. Their presence would also be indicated in the hexabromide test, if the yield of the hexabromides of the mixed acids falls below 25 per cent. Since tung oil and poppy seed oil yield no hexabromides, safflower and walnut oils a very small quantity only, and candle nut oil less than half of the quantity to be expected from linseed oil, the hexabromide test will be found of greater help than the iodine test.

Cotton Seed Oil.—An inducement to adulterate linseed oil with cotton seed oil will only present itself whenever the latter oil is cheaper than linseed oil. The presence of cotton seed oil would be detected by a low iodine value. The *Halphen* colour test should be applied as a confirmatory test (see p. 530), and the melting point of the fatty acids should be determined. In the presence of considerable quantities of cotton seed oil, the titer test will lie considerably below 20° C.

Rape oil would be indicated by a lower saponification value than a normal one (of course, in the absence of unsaponifiable oils). A few per cent of rape oil, such as are frequently present in commercial linseed oil, will not be detected thereby. The test will, however, in many cases afford some guidance as to the excess of foreign seeds in the linseed from which the sample has been obtained.

Fish Oils.—Since fish oils absorb fully as much iodine as linseed oil does, and since they yield as much and even more hexabromides than linseed oil, the quantitative tests will not give a satisfactory answer.

More decisive results are obtained by taking the melting point of the hexabromide of the fatty acids. In the case of pure linseed oil, a white or only slightly yellowish hexabromide is obtained, melting sharply without decomposition at 175°-180° C., whereas the hexabromides from fish and blubber oils become dark or almost black at 200° C., and do not melt. Even 10 per cent of fish oil can thus be detected. In doubtful cases the most reliable test for the presence of fish, liver, and blubber oils is the phytosteryl acetate test. The crystals of phytosteryl acetate from pure linseed oil melt at 128°-129° C. (*Bömer* and *Winter*). In presence of cholesterol much lower melting points are obtained.

Unsaponifiable Matter.—Adulteration with mineral oils and rosin oils is still frequently practised, although these oils are very easily detected. If only one of these two oils be the adulterant used, the specific gravity of the sample alone will indicate the further line of examination. A judiciously prepared mixture of both oils will, however, have the proper specific gravity of linseed oil. The presence of either adulterant is readily indicated by the saponification value (below 190), and the amount of the adulterant is determined by ascertaining the unsaponifiable matter. Pure linseed oils contain no more than 1-2 per cent of unsaponifiable matter. If a notable amount of unsaponifiable matter has been found, and the presence of rosin oil be suspected, the polarimetric method will give useful indications. Linseed oil is practically optically inactive—a sample of East India oil, examined in a 200 mm. tube, showed the deviation of 0° 6′ to the right—whereas rosin oil is strongly dextro-rotatory.

Rosin (colophony) is best detected qualitatively by applying the *Liebermann-Storch* reaction. If the colour of the sample be very dark, it is best to warm it with alcohol so as to extract the bulk of the colophony, and to test the alcoholic extract. The amount of rosin can be determined quantitatively by titrating the sample of oil with aqueous normal alkali, using phenolphthalein as an indicator. From the amount so found, there must be subtracted the amount of alkali used for neutralising the free fatty acid in linseed oil—rarely exceeding about 3 per cent. Test experiments made in my laboratory with mixtures of linseed oil and rosin prove the correctness of this method. If, however, a large amount of linseed oil fatty acids is present, as in linseed oil soap stock (see above), the amount of rosin in the alcoholic extract must be determined quantitatively by *Twitchell's* method (p. 394).

Linseed oil is very extensively used as stock material for soft soaps; for this purpose those oils are especially employed which have a comparatively low iodine value. The presence of mucilage forms no objection.

The principal application of linseed oil is found in the manufacture of boiled oil for paint, varnishes, for lithographic varnishes, and for the manufacture of linoleum. No other drying oil approaches the properties of linseed oil, the drying oil *par excellence.*

Linseed oil is also used in the manufacture of "Vulcanised Oils" (cp. however, chap. xv.). By heating linseed oil with sulphur, the official *oleum lini sulf.* is prepared.

The manufacture of **boiled oil**, its characteristics, and detection if in admixture with linseed oil, will be treated of in Chapter XV.

TUNG OIL

(*Chinese Wood Oil, Japanese Wood Oil*)[1]

French—*Huile de bois.* German—*Tungoel, Oelfirnissbaumoel.*
Italian—*Olio di legno del Giappone.*

For tables of constants see pp. 465, 466.

Tung oil is obtained from the seeds of *Aleurites cordata* (*Elæococca vernicia, Dryandra cordata*), a tree indigenous to China and Japan. (Japanese, *Abura giri, Jani, Kiri;* Chinese, *Tung Yu.*)

Tung oils vary somewhat according to their source. The seeds are treated in different localities in a different manner. They are frequently divided into three kinds—yellow, drab, and white. The seeds are roasted in a flat dish over a naked fire, and then broken to powder between stones; finally the mass is expressed in crudely made wooden presses. The seeds contain about 53 per cent of oil, but the yield of oil amounts to only 40-41 per cent. The cold drawn oil is pale yellow, and termed white tung oil. This is the variety chiefly imported into Europe. The oil obtained by hot pressing is dark brown, and termed black tung oil, and is consumed at home. This

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[1] The oil is also known in commerce under the name wood oil, but since Gurjun balsam is also termed wood oil, confusion of tung oil with the ethereal Gurjun oil must be avoided.

oil has an unpleasant taste, and its odour is more pronounced than that of the white tung oil, which is also somewhat unpleasant. This odour precludes its use for many purposes.

Tung oil is also expressed in Madagascar, where the oil is known under the name "Bakoly oil."

The chief shipments of oil are made from Hankow and Wuchow in China; comparatively smaller quantities are shipped from Japan.

Tung oil consists chiefly of the glycerides of oleic and elæomargaric acids (p. 113). Hence, although tung oil gives in the hexabromide test 0·38 per cent of a precipitate, its fatty acids did not yield any linolenic hexabromide (cp. chap. viii.). In the elaïdin test an oily layer is obtained resting on the lower, nearly solid product; when stirred up, the whole mass flows. The characteristic numbers are contained in the two tables, therefore it is only necessary to point out the special properties serving to identify this oil.

The freshly expressed oil is free from fatty acids; the samples examined in Europe contain from 4-6 per cent of free fatty acids, calculated as oleic acid. The amount of unsaponifiable matter in the tested samples did not exceed 0·5 per cent.

The oil is most readily identified by its strong characteristic smell, which is not easy to remove. The Chinese variety of tung oil is also characterised by having the highest specific gravity of any known oil with the exception of castor oil, with which of course it cannot be easily confounded. The Japanese variety of tung oil has a lower specific gravity, viz., 0·933-0·935 at 15·5° C.

The oil is further readily recognised by the manner in which it dries; it possesses even more strongly pronounced drying power than linseed oil. It differs, however, from it in that it gives on a glass plate a dry opaque skin, which is wax-like, but has no elasticity, and hence is not useful commercially.

Hall[1] states that he once obtained a sample of tung oil giving a most beautiful thin transparent film.

When heated with lead oxide in red lead, the oil gelatinises within fifteen minutes to a light brown mass.

A characteristic property of tung oil is to form a jelly on being heated to 250° C. for a short time, or even when kept at 180° C. for an hour or two. The jelly-like mass so obtained possesses some elasticity, is insoluble in the ordinary solvents of oil, and shows no tendency to melt on being again heated to 250° C. The gelatinisation is not due to oxygen absorption, as has been explained by some observers, since the conversion into a semi-solid mass takes place when air is carefully excluded. Further study of the properties of elæomargaric acid, which distinctly differs from linolic acid, may lead to a proper explanation of the curious behaviour of this oil on heating. The change is very likely due to polymerisation of the glycerides.

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[1] *Journ. Soc. Chem. Ind.* 1903, 599.

Physical and Chemical Constants of Tung Oil

Specific Gravity.			Solidifying Point.[4]		Saponification Value.		Iodine Value.		Helmer Value.		Thermal Tests. Maumené Test.		Refractive Index. Oleo-refractometer.	
At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	Per cent.	Observer.	Specific Temp. Reaction.	Observer.	"Degrees" at 22° C.	Observer.
15	0·936[1]	De Negri and Sburlati	Below −17	Jenkins	211	Davies and Holmes	165·7	Jenkins	96·4	Jenkins	372	Jenkins[6]	+75	Pearmain
											298	,,		
15·5	0·9385	Jenkins			194	Jenkins	149·7	,,	96·0	,,				
,,	0·9343	,,			192	,,	159 161	De Negri and Sburlati	96·3-96·66	Williams				
,,	0·9412-0·9418[2]	Lewkowitsch			155·6[5]	De Negri and Sburlati	163·4	Lewkowitsch			Heat of Bromination. °C.		Refractive Index.	
,,	0·933-0·935[3]	Nash			172 191·2	,, Deering	155·4-165·6	Williams			23·4	Jenkins	At 19° C.	Observer.
					190·7-196·1	Williams	163	Zucker			21·4	,,		
					197	Zucker					26·7-27·6	Williams	1·503	Jenkins

[1] Prepared in the laboratory from the seeds. [2] Chinese oil. [3] Japanese oil.

[4] According to De Negri and Sburlati, tung oil obtained by expression solidifies at 2°-3° C., whereas oil extracted by means of carbon bisulphide, after heating to 100° C., yields a crystalline mass solidifying at 32° C. and melting at 34° C. Cloëz (*Compt. rend.* 81, 469), who first observed this phenomenon, explains this by the formation of elæostearin.

[5] Commercial oil. [6] 10 grms. of the sample diluted with 40 grms. of olive oil.

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.		Thermal Test. Heat of Bromination.	
°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.
34	Jenkins	37	Jenkins	188·8	De Negri and Sburlati	150·1	Jenkins	21·0	Jenkins
31·2	De Negri and Sburlati[1]	30-31	,,			144·1	,,		
		43·8	De Negri and Sburlati[1]			159·4	De Negri and Sburlati[1]		
		40	Williams						
Titer Test.						Liquid Fatty Acids.			
37·1-37·2	Lewkowitsch					145·0	Lewkowitsch		

Tested in *Redwood's* viscosimeter, 50 c.c. of the oil required 1433 seconds as compared with 28 seconds for water.

In **Valenta's test** the temperature of turbidity is 44°-47° C.

In the **sulphur chloride test** 5 grms. of the oil treated in the cold with 2 c.c. of S_2Cl_2 and 2 c.c. of CS_2 give in 1½ minutes a thick, stiff jelly. (This does not take place when tung oil is adulterated with Gurjun balsam, the ethereal oil of *Dipterocarpus turbinatus Zucker*[2]). The **refractive index** of tung oil is much higher than that of any known fatty oil. It should be noted that it cannot be examined in the butyro-refractometer, since its refraction would place it beyond the 100 degree limit of this instrument (as in the case of rosin oils).

If a saturated solution of iodine in chloroform or any other solvent be dropped on tung oil, the oil is immediately solidified; and if the oil has been previously dissolved in chloroform, a jelly is obtained. Bromine has no such action on the oil.

Concentrated sulphuric acid gives a black clot with the oil. When 1 grm. of the oil is dissolved in 5 c.c. of chloroform, and 5 c.c. of a saturated solution of iodine in chloroform is added and the mixture stirred, the whole is converted into a stiff jelly after about 2 minutes. If 2 grms. of the oil be employed under the same conditions, the jelly is so stiff that it can be granulated.

Statements that tung oil is being adulterated with cotton seed oil have not been borne out by the author's experience. Commercial samples examined in this direction have shown throughout the absence of cotton seed oil. A lower iodine number than those registered in the table will readily reveal the presence of cotton seed oil.

Tung oil, on account of its drying properties, might suggest itself as an adulterant of linseed oil, but although it is the most

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[1] Prepared in the laboratory from seeds.

[2] *Chem. Zeit. Repert.* 1900, 156.

rapid drying oil known hitherto, it cannot replace linseed oil. In fact, even in Japan itself, linseed oil has not been ousted by tung oil, except for some common purposes, such as paper umbrellas (*Divers*[1]). A few years ago, when tung oil (which is being produced in enormous quantities) was shipped in large quantities to Europe, and was therefore somewhat strongly pressed on the market, a large number of patents were taken out purporting to put tung oil to the same uses as linseed oil, or at least to employ it in admixture with linseed. Yet hitherto very little progress has been made in the technical application of tung oil.

Further information will be given under "Polymerised Oils" and "Oxidised Oils" in Chapter XV.

In China and Japan tung oil is used chiefly as a natural varnish for wood, for caulking junks and boats, and also for lighting. The cold drawn oil is stated to be used in medicine as an emetic and also as a purgative.

LALLEMANTIA OIL[2]

French—*Huile de Lallemantia.* German—*Lallemantia Oel.*
Italian—*Olio di lallemanzia.*

Physical and Chemical Constants of Lallemantia Oil

Specific Gravity at 20° C.	Solidifying Point.	Saponification Value.	Iodine Value.	Reichert Value.	Hehner Value.
0·9336	–35° C.	185	162·1	1·55	93·3

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.	Melting Point.	Iodine Value.
11° C.	22·2° C.	166

Lallemantia oil is obtained from the seeds of *Lallemantia iberica*, a plant belonging to the *Labiatæ*, growing wild in the Caucasus, and cultivated in Russia (near Kieff).

The oil belongs to the best drying oils, as is indicated by its iodine value. A sample of the oil spread on a watch-glass dried after 9 days to a thick, resin-like skin. If the oil was heated to 150° C.

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[1] *Journ. Soc. Chem. Ind.* 1903, 599.
[2] Richter, *Zeitsch. f. Chem. Ind.* 1887, 230.

for 3 hours, complete drying took place after 24 hours. The absorption of oxygen, determined according to *Livache*, using copper powder, was 15·8 per cent after 24 hours for the oil, and 14 per cent after 8 days for the mixed fatty acids. 10 grms. of the oil at 18° C. mixed with 2 grms. of concentrated sulphuric acid rose to a temperature of 120° C.

In the elaïdin test 10 grms of the oil, 5 grms. of nitric acid, specific gravity 1·4, and 1 grm. of mercury, gave after shaking for 3 minutes a dark-red dough-like mass.

Lallemantia oil is used for illuminating purposes. It may find technical application as a substitute of linseed oil in the preparation of varnishes.

CANDLE NUT OIL

French—*Huile de noix de chandelle.* German—*Candlenussoel, Bankulnussoel.* Italian—*Olio die noci di Bankoul.*

For tables of constants see p. 469.

Candle nut oil is obtained from the seeds of *Aleurites moluccana, Willd.*, a tree widely distributed in the South Sea Islands. The fruits resemble ordinary walnuts in their appearance; their shell is, however, far thicker. The shell is removed by the natives in a primitive fashion by drying the nuts on hot stones, so that the shell can be readily broken by a slight blow with a hammer. The seeds contain 62·25 per cent of oil.

In view of the divergent numbers—especially as regards the iodine value—recorded in the table of constants, it may be pointed out that the writer prepared the oil on a semi-large scale from seeds obtained from a reliable source in the South Sea Islands. Hence the numbers given by *Lewkowitsch*[1] must be accepted as the more correct ones. (Practically identical numbers have been obtained by *Kassler*[2] from Fiji candle nuts, the seeds of which contained 58·6 per cent of oil.) The oil cakes obtained on a large scale by expressing the oil from the crushed nuts had the following composition:—

	Per cent.
Oil	8·80
Moisture	10·00
Ash	8·28
Albuminoids	46·16
Cellulose	1·47
Carbohydrates (by difference)	25·29

The ash contained 23·52 per cent potassium oxide, and 53·04 per cent phosphorus pentoxide.

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[1] *Chem. Revue*, 1901, 156.

[2] *Augsburger Seifensieder Zeitung*, 1902, 689.

Physical and Chemical Constants of Candle Nut Oil

Specific Gravity.			Melting Point.		Saponification Value.		Iodine Value.		Hehner Value.		Refractive Index. Butyro-refractometer.		
At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	Per cent.	Observer.	At °C.		Observer.
15	0·9232	Cloëz	Liquid at – 18°	De Negri	184-187·4	De Negri	136·3-139·3	De Negri	95·5	Lewkowitsch	15	76-75·5	De Negri
15	0·920-0·926	De Negri			192·62	Lewkowitsch	163·7	Lewkowitsch			20	78·5	Lewkowitsch
15·5	0·92565	Lewkowitsch									25	76·0	,,

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.
13	De Negri	20-21	De Negri	142·7-144·1	De Negri
				Liquid Fatty Acids.	
				185·7	Lewkowitsch

The cold drawn oil is limpid, colourless, or yellowish, has a pleasant odour and bland taste, but cannot be used for edible purposes on account of its purging properties.

Although the seeds were examined several months after arrival, the extracted oil contained only 4 per cent free fatty acids. Its acetyl value was 9·86, and the proportion of oxidised acids 0·21 per cent.

The high iodine value places the oil prominently amongst the drying oils. However, the older statements that this oil surpasses linseed oil in drying properties must be abandoned as erroneous; not only is its iodine value lower than that of linseed oil, but the proportion of hexabromides is much smaller. Thus *Walker* and *Warburton*[1] ascertained in the writer's laboratory that the oil yields from 7·28 to 8·21 per cent of hexabrominated glycerides, whilst the fatty acids yield from 11·23 to 12·63 per cent hexabrominated acids.

Candle nut oil is obtainable in enormous quantities. It is used in its home as a burning oil. It should prove suitable for soap-making, especially for the manufacture of soft soaps. It may also find some application in the manufacture of paint oils and varnishes as a substitute for linseed oil. When the price of linseed oil is high, adulteration with candle nut oil may occur. Its presence would be revealed by a somewhat low iodine value of the sample, and a low yield of hexabromides. Smaller quantities than 20 per cent could, however, not be detected by chemical means. In doubtful cases practical drying tests must be resorted to.

Oil obtained from *Aleurites triloba* is known in India under the name of

KEKUNA OIL[2] (CANDLE NUT OIL)

The yield of the oil from the seeds is about 50 per cent. The roasted nut forms an agreeable fruit.

The oil is used for soap making and cloth dressing.

STILLINGIA OIL[3] (TALLOW SEED OIL)

French—*Huile de Stillingia.* German—*Stillingiaoel.*
Italian—*Olio di Stillingia.*

For tables of constants see p. 471.

Stillingia oil is obtained from the seeds of *Stillingia sebifera* (*Croton sebiferum*), *Sapium sebiferum*, and is contained therein to the extent of 19·2 per cent. The mesocarp surrounding the seeds yields, on being steamed, the vegetable tallow of China (cp. p. 729). The oil is obtained by expressing the seeds after freeing them from the vegetable tallow; the oil is termed by the natives tsé-iéou or ting-yu.

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[1] *Analyst*, 1902, 237.

[2] *Journ. Soc. Chem. Ind.* 1901, 642.

[3] "Oleum stillingiæ" is vegetable tallow (of China).

Physical and Chemical Constants of Stillingia Oil

Specific Gravity.			Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Hehner Value.		Thermal Test.		Refractive Index.	
													Butyro-refractometer.	
°C.		Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	Maumené. °C.	Observer.	"Degrees" at 35° C.	Observer.
15	0·9458	Hobein	203·8	Hobein	145·6	Hobein	0·93	Tortelli and Ruggeri	94·4	Tortelli and Ruggeri	136·5[1]	Tortelli and Ruggeri	75	Tortelli and Ruggeri
15·5	0·9395	Nash	210·4	Tortelli and Ruggeri	160·6	Tortelli and Ruggeri								
15 (water 15° = 1)	0·9432	Tortelli and Ruggeri			160·7	Nash								
27 (water 15° = 1)	0·9370	,,									Spec. Temp. React.		Refractive Index. At 23·5° C.	
100 (water 15° = 1)	0·8737	,,									267	Tortelli and Ruggeri	1·4825	Nash

[1] Jean's thermelæometer.

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
12·2 (Titer Test)	Tortelli and Ruggeri	14·5	Tortelli and Ruggeri	214·2	Tortelli and Ruggeri	161·9	Tortelli and Ruggeri
				206·3	Lewkowitsch	181·8	Lewkowitsch
				210·5 (saponification value)	,,	165·0	Nash
						Liquid Fatty Acids.	
						178·1	Tortelli and Ruggeri
						191·1	Lewkowitsch

The oil is limpid and of pale yellow colour, and has a peculiar smell resembling that of linseed oil and mustard.

The fatty acids separate into a liquid and solid portion. A specimen of mixed fatty acids examined in my laboratory yielded 25·78 per cent of hexabromides of a melting point 171·1° C. (*Lewkowitsch*).[1]

The specimen prepared by *Tortelli* and *Ruggeri* contained 6·15 per cent of free fatty acids (calculated to oleic acid) and 1·45 per cent unsaponifiable matter. A specimen examined by *Nash*[2] contained 3·1 per cent free fatty acids and 0·44 per cent of unsaponifiable matter. 1000 grms. absolute alcohol dissolve at the ordinary temperature 42·8 grms. of the neutral oil, or 48·9 grms. of the oil containing 6·15 per cent free fatty acids.

The most characteristic property of the oil is that it rotates strongly the plane of polarised light to the left, viz. – 6° 45′ in a 200 mm. tube in a *Laurent* polarimeter, corresponding to – 29·9 saccharimeter degrees. The optical activity of the oil is confirmed by *Nash*.

Stillingia oil is a very good drying oil, absorbing 8·72 per cent and 12·45 per cent of oxygen after two and eight days respectively in *Livache's* test.

WHITE ACACIA OIL[3]

German—*Weiss-Akazienoel.*

This oil has been obtained from the seeds of the white acacia, *Robinia pseudacacia*, cultivated in South Russia. On extraction with petroleum ether, the seeds yielded 13·3 per cent of oil.

Physical and Chemical Constants of White Acacia Oil

Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Hehner Value.
192·4	161·0	1·2	94·32

Physical and Chemical Constants of the Mixed Fatty Acids

Neutralisation Number.	Mean Molecular Weight.	Iodine Value.
200·1	280·4	160·7

The specimen contained 0·20 per cent of unsaponifiable matter. The oil possesses strong drying power, as indicated by its high iodine

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[1] *Analyst*, 1904, 112.
[2] *Analyst*, 1904, 111.
[3] Valentin Jones, *Mittheil. k. k. technolog. Gewerbe-Museum*, 1903, 223.

value. From the total mixed fatty acids, 3·7 per cent of solid fatty acids were obtained; amongst these were identified stearic and erucic acids. The liquid fatty acids consist of oleic, linolic, and linolenic acids, linolic acid predominating. The oil is easily oxidised on exposure to the air.

CEDAR NUT OIL

French—*Huile de noix de cèdre.* German—*Cedernussoel.*
Italian—*Olio di noce di cedro.*

For tables of constants see p. 474.

Cedar nut oil is obtained from the nuts of the Siberian cedar or stone pine (*Pinus cembra*), a tree forming large forests in Southern Siberia. The oil belongs to the fir seed oils, but on account of its very high iodine value as compared with the iodine values of the other fir seed oils, it is preferable to describe it separately.

The oil has a golden-yellow colour and a pleasant taste. In cold carbon bisulphide and in cold benzene it is soluble with difficulty, but dissolves easily on warming.

Amongst the solid acids, palmitic acid was identified; the liquid fatty acids consist chiefly of linolic acid. Oleic and linolenic acids are only present in small quantities. The unsaponifiable matter in the specimen examined by *v. Schmoelling* was 1·3 per cent; the acetyl value of the fatty acids after six days' standing was 81·9.

The oil is used in Siberia as an edible oil.

[Table

Physical and Chemical Constants of Cedar Nut Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Hehner Value.		Maumené Test.	
At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.
0	0·932	Kryloff[1]	−20	Kryloff	191·8	Kryloff	149·5-150·5	Kryloff	2·0	Kryloff	93·33	Kryloff	98[3]	v. Schmoelling
15	0·930	v. Schmoelling[2]			191·8	v. Schmoelling	159·2	v. Schmoelling	3·77 per cent volatile acids	v. Schmoelling	91·97	v. Schmoelling		

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[1] *Journ. Soc. Chem. Ind.* 1899, 501.

[2] *Chem. Zeit.* 1900, 815.

[3] By Archbutt's method.

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.	Neutralisation Value.	Mean Molecular Weight.	Iodine Value.	Observer.
°C.	Mgrms. KOH.		Per cent.	
11·3	193	290	161·3	v. Schmoelling
			Liquid Fatty Acids.	
			184	

HEMP SEED OIL

French—*Huile de chènevis.* German—*Hanfoel.*
Italian—*Olio di canapa.*

For tables of constants see p. 476.

Hemp seed oil is obtained from the seeds of the hemp plant, *Cannabis sativa.* The colour of the freshly expressed oil is light green to greenish-yellow, becoming brownish-yellow on keeping. The solid glycerides in hemp seed oil are stated to consist of stearin and palmitin; very likely stearin is absent. The liquid fatty acids in hemp seed oil are, according to the researches of *Bauer*, *Hazura*, and *Grüssner*, linolic acid and smaller quantities of oleic, linolenic, and isolinolenic acids.

Pure hemp seed oil may be easily identified by its high iodine absorption.

Hemp seed oil is used as a paint oil, though less frequently in this country than on the Continent. Considerable quantities are employed on the Continent for making soft soaps, characterised by a dark green colour. The lower qualities of hemp seed oil are also used in the manufacture of varnishes.[1]

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[1] Lidoff, *Chem. Revue*, 1900, 120.

[TABLE

Physical and Chemical Constants of Hemp Seed Oil

Specific Gravity.		Solidifying Point.	Saponification Value.		Iodine Value.		Maumené Test.		Refractive Index. Oleo-refractometer.	
At 15° C.	Observer.	°C.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.	"Degrees."	Observer.
0·925-0·931	Allen	Thickens at −15 and solidifies at −27	193·1	Valenta	157·5	Benedikt	98	Maumené	+30 to +34	Jean Pearmain
0·9270	Chateau		192·8	De Negri and Fabris	140·5	De Negri and Fabris	95-96	De Negri and Fabris	+34 to +37·5 at 22° C.	
0·9255	Massie									
0·9280	De Negri and Fabris		190-191·1	Lewkowitsch	148	Lewkowitsch				

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer
15	Hübl	19	Hübl	122·2-125·2	Morawski and Demski
16 14-15	De Negri and Fabris	18-19 17-18	De Negri and Fabris	141	De Negri and Fabris
Titer Test. 15·6-16·6	Lewkowitsch				

WALNUT OIL—NUT OIL

French—*Huile de noix.* German—*Nussoel, Wallnussoel.*
Italian—*Olio di noce.*

For tables of constants see pp. 478, 479.

This oil is obtained from the seeds of the common walnut tree, *Juglans regia.* The fruit intended for the preparation of the oil must be allowed to ripen fully and be kept two to three months before being pressed, as the fresh seeds yield a very turbid oil, difficult to clarify. The kernels contain from 63 to 65 per cent of oil. The cold-drawn oil is almost colourless, or of a pale, yellowish-green tint, and has a pleasant smell and an agreeable nutty taste; the hot-pressed oil has a greenish tint and an acrid taste and smell.

The solid glycerides of walnut oil are stated to contain myristic and lauric acids; the liquid fatty acids of the oil consist chiefly of linolic acid, and of smaller quantities of oleic, linolenic, and isolinolenic acids. *Hehner* and *Mitchell* obtained from 1·42 to 1·9 per cent hexabrominated glycerides in the hexabromide test. The statement made by *Kebler*[1] that a sample of walnut oil had the *Reichert-Meissl* value 15, requires confirmation; all the more so as the saponification value of the sample was found to be 190·1 to 190·5.

One part of walnut oil dissolves in 188 parts of cold, or in about 60 parts of boiling alcohol. On cooling, crystals separate from the solution.

Walnut oil is a very good drying oil. Its comparatively high price acts as an incentive to adulterate it with linseed oil. The latter is detected by a higher **iodine value** than the normal one. Presence of other vegetable oils, such as *sesamé* oil, *arachis* oil, is recognised by the lower iodine absorption. Walnut oil, in its turn, is used as an adulterant for olive oil, its higher iodine absorption being compensated by the addition of lard oil.

The best qualities of walnut oil are almost colourless; such oil is therefore preferred to any other oil for the making of white paints for artists. These paints are less liable to crack than the paints made with linseed oil. Poppy seed oil, which is also used in the preparation of white paints for artists, is differentiated from walnut oil by not yielding any hexabrominated glycerides in the hexabromide test. Walnut oil containing notable amounts of free fatty acids is unsuitable for making paints; such oil finds an outlet in the manufacture of soft soaps.

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[1] *Amer. Journ. Pharm.* 1901, 73, 173.

[TABLE

Physical and Chemical Constants of Walnut Oil

Specific Gravity.			Solidifying Point.	Saponification Value.		Iodine Value.	
At °C.		Observer.	°C.	Mgrms. KOH.	Observer.	Per cent.	Observer.
12	0·928	Saussure	Thickens at −12 and solidifies at −27·5	196·0	Valenta	143	Hubl
15	0·925-0·926	Allen		188·7	Dieterich	147·9-151·7	Dieterich
15	0·9265	De Negri and Fabris		194·4	Maben	145·7	Hazura
15	0·9256	Blasdale[1]		193·81-197·32	De Negri and Fabris	147·92-148·4	Petkow[2]
15·5 (water 15·5=1)	0·9259	Crossley and Le Sueur		194·4	Blasdale	143·3	Peters
25	0·919	Saussure		192·5	Crossley and Le Sueur	144·5-145·1	De Negri and Fabris
94	0·871	,,				132·1	Blasdale
						143·1	Crossley and Le Sueur

Physical and Chemical Constants of Walnut Oil—continued

Reichert-Meissl Value.		Hehner Value.		Maumené Test.		Refractive Index.			Viscosity in Redwood's Viscosimeter.	
c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.			Observer.	Seconds at 70° F.	Observer.
0·00	Crossley and Le Sueur	95·44	Crossley and Le Sueur	101	Maumené	1·4804		Blasdale	231·8	Crossley and Le Sueur
				96	De Negri and Fabris	Oleo-refractometer.				
				110	Blasdale	"Degrees."		Observer.		
						+35 to +36		Jean		
						Butyro-refractometer.				
						At °C.		Observer.		
						40	64·8	Crossley and Le Sucur		
						40	67-68	Petkow[2]		

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[1] Blasdale (*Journ. Soc. Chem. Ind.* 1896, 206). Oil from *Juglans regia* grown in California.

[2] Five samples of cold-pressed oil.

[TABLE

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.	
° C.	Observer.	° C.	Observer.	Per cent.	Observer.
16	Hübl	20	Hübl	150·05	De Negri and Fabris
		16-18	De Negri and Fabris	Liquid Fatty Acids.	
		15	Blasdale	167	Tortelli and Ruggeri

SAFFLOWER OIL—SAFFRON OIL

French—*Huile de Carthame.* German—*Safloroel.*
Italian—*Olio di cartamo.*

For table of constants see p. 482.

Safflower oil is obtained from the seeds of *Carthamus tinctorius*, a plant until recently cultivated all over India for the preparation of the dye. The chief localities where the plant is grown are Bengal, Hyderabad, Cawnpore, Bombay, and the Punjab. Two distinct varieties of the plant were grown, *Carthamus tinctorius* and *Carthamus oxyacantha.* The cultivation of the plant has also been extended to the Caucasus and Turkestan, and seems to be on the increase in these countries. The seeds contain from 30 to 32 per cent of oil, but owing to the thick husk, only 17 to 18 per cent of the oil are obtainable by pressing. The press cake contains, therefore, a large amount of woody fibre, as shown by the following analysis of a pressed cake, prepared by the writer on a semi-large scale.

	Per cent.
Albuminoids	20·11
Oil	11·91
Starch, sugar, etc.	10·83
Woody fibre	40·75
Moisture	11·60
Ash	4·80

This analysis points to the necessity of first decorticating the seeds, so as to lay bare the kernel which forms 40 per cent of the seed. Special machinery is required for decorticating the seeds, the ordinary Anglo-American rollers having been found unsuitable on account of the extreme hardness of the husk. An experiment carried out on a semi-large scale[1] with a special machine yielded over 31 per cent of kernels (" meats ").

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[1] Cp. Lewkowitsch, "Problems in the Fat Industry," *Journ. Soc. Chem. Ind.* 1903, 590.

The oil is prepared in India on a small scale from two kinds of fruits—the cultivated white and glossy form, and the small fruit of a mottled brown, gray, or white appearance. The oil obtained from the cultivated variety by expression in the cold is pale yellow; it has a pleasant taste approaching that of sunflower oil, so that it can be largely used as an edible oil. Considerable quantities are pressed in India together with other seeds, especially arachis nuts.

The saturated fatty acids contained in safflower oil consist of palmitic and stearic acids, as ascertained by fractional precipitation with magnesium acetate of those acids which yield lead salts insoluble in ether. The high iodine value of the oil points to large amounts of unsaturated acids. *Le Sueur*, examining the oil by the oxidation and bromination methods, states that the liquid fatty acids consist of oleic and linolic acids; no evidence of the presence of linolenic acids was obtained. *Walker* and *Warburton*, however, ascertained in the writer's laboratory [1] that whilst the oil yields no hexabromo-glycerides, the fatty acids give from 0·65 to 1·65 per cent linolenic hexabromides. *Tylaikoff* confirms the presence of oleic and linolenic acids, he having obtained the oxidation products of these two acids; the same observer proved also the occurrence of linolic acid by isolating tetrabromostearic acid after brominating the acids. The unsaponifiable matter in several specimens of oil examined in my laboratory amounted to 1·5 per cent. In view of the importance this oil may acquire, a number of analyses, which have been summarised partly in the table of constants, may be added here.

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[1] *Analyst*, 1902, 237.

[TABLE

Indian Safflower Oils (*Crossley and Le Sueur*[1])

Name.	Description.	Source.	Specific Gravity.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Hehner Value.	Refractive Index at 40° C.	Viscosity.		Acid Value.	Optical Activity in 200 mm. tube.
								Butyro-refractometer.	Seconds at 70° F.	Compared with Water.		
Carthamus tinctorius	...	C. Provinces	0·9267	192·50	140·05	...	95·30	65·2	256·1	10·08	10·41	+8′
,, ,,	Pressed oil	Bengal	0·9264	193·30	144·40	...	...	...	247·8	9·76	3·68	+7′
,, ,,	...	Punjab	0·9275	186·60	138·64	0·00	...	...	274·5	10·81	8·28	...
,, ,,	From cultivated form	,,	0·9267	189·60	144·05	...	...	...	249·1	9·81	0·76	+10′
,, ,,	From wild form	,,	0·9253	187·40	129·80	...	...	...	...	...	2·90	+12′
,, ,,	By cold dry expression	Hyderabad	0·9277	187·90	138·60	...	...	...	274·7	10·79	2·58	+14′
,, ,,	From dye plant	Bombay	0·9262	187·20	143·40	...	...	65·2	250·3	9·85	2·67	+8′
,, ,,	From oil seed plant	,,	0·9269	191·30	149·93	0·00	...	...	249·6	9·83	6·20	+4′
,, ,,	Var.: Thornless	Cawnpore	0·9271	189·40	141·42	0·00	...	...	258·8	10·19	5·92	+7′
,, ,,	Var.: Thorny	,,	0·9251	190·52	141·12	...	...	...	243·0	9·57	20·02	...
,, ,,	...	Madras	0·9280	192·42	142·85	...	...	...	268·8	10·58	4·12	+6′
,, oxyacantha	...	Punjab	0·9270	189·40	135·49	...	95·44	...	294·0	11·57	3·66	+7′

Safflower oil is heated by the natives to obtain an oil suitable for the preservation of leather vessels, ropes, etc., exposed to the action of water. A specimen of oil thus prepared (cp. p. 483) had the specific gravity 0·9634, the saponification value 188·0, and the iodine value 128·9. It thus represents a kind of "boiled oil."

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[1] *Journ. Soc. Chem. Ind.* 1898, 991.

Physical and Chemical Constants of Safflower Oil

Specific Gravity.			Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Hehner Value.		Refractive Index.		Viscosity in Redwood's Viscosimeter.	
At °C.		Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	cc. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	At 16°C.	Observer.	Seconds at 70° F.	Observer.
15·5 (water at 15·5° C. = 1)	0·9251-0·9280	Crossley and Le Sueur	186·6-193·3	Crossley and Le Sueur	129·8-149·9	Crossley and Le Sueur	0·0	Crossley and Le Sueur	95·4	Crossley and Le Sueur	1·477	Tylaikoff	249·1-294	Crossley and Le Sueur
,,	0·9274	Lewkowitsch	192·2	Lewkowitsch	146·5	Lewkowitsch	1·45-1·63	Jones					235	Lewkowitsch
,,	0·9246	,,	190·0	,,	147·3	,,	0·69-0·88	Tylaikoff			Butyro-refractometer at 40° C.			
,,	0·9250	Tylaikoff	194	Tylaikoff	143-144·5	Jones[1]					65·2	Crossley and Le Sueur		
20	0·9277	Jones[1]	194·4	Jones[1]										

Titer Test of the Mixed Fatty Acids, 16° C. (*Lewkowitsch*).

Iodine Value of the Liquid Fatty Acids, 159·6 (*Lewkowitsch*).

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[1] *Chem. Ztg.* 1900, 272.

[2] *Journ. Soc. Chem. Ind.* 1900, 104.

Safflower oil is a good drying oil, and although it cannot replace linseed oil in all its applications, it should certainly be a good substitute for it in many instances, and find extended use in the manufacture of soft soap. In *Livache's* test the oil absorbed 6·4 per cent of oxygen after two days (*Tylaikoff*).

A special process of preparing a kind of "boiled oil" is carried out in India as follows:—The seeds of the wild safflower, *Carthamus oxyacantha*, are expressed in the hot, and the oil is boiled in earthenware vessels for twelve hours, during which time considerable quantities of acroleïn volatilise. The "boiled" oil is immediately placed into flat dishes, partly filled with cold water, so that the oil solidifies to a jelly-like thick mass termed "roghan" (Afridi wax). This "boiled oil" is employed by the natives in Lahore, Delhi, Bombay, and Calcutta for the manufacture of "Afridi wax linoleum." It is also used by the natives for drawing artistic designs on woven cloth, the production of which was considered for a long time a valuable secret. The pattern is made by the natives by means of finely pointed staves dipped in the "roghan" which is drawn in very fine threads, and so deposited on the cloth. When completely dry, it forms an indelible pattern.

ECHINOPS OIL (THISTLE SEED OIL)

German—*Echinopsoel.*

This oil is obtained from the seeds of *Echinops ritro*, a plant belonging to the family of *Compositæ*, and indigenous in Asia and the Mediterranean; the yield of oil from the seeds is 27·5 per cent.

The constants found by *Wijs*[1] on examining two specimens of the oil, containing 4·4 per cent and 7·3 per cent of free fatty acids respectively, are given in the following tables.

The oil absorbs 9 per cent of oxygen (*Weger's* method), 1000 c.c. of absolute alcohol at 15° C. dissolve 51 grms. of the neutral oil (freed from fatty acids). The acetyl value of one specimen was found to be 26·5.

The oil gives neither the *Halphen* nor the *Baudouin* reaction.

Physical and Chemical Constants of Echinops Oil

Specific Gravity.	Saponification Value.	Iodine Value.
At 20° C. (Water 4° = 1.)	Mgrms. KOH.	Per cent.
0·9285-0·9253	189·2-190	138·1-141·2

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[1] *Zeit. f. Nahrgs. und Gesussm.* 1903, 492.

Physical and Chemical Constants of the Mixed Fatty Acids

Melting Point.	Neutralisation Value.	Mean Molecular Weight.	Iodine Value.
°C.	Mgrms. KOH.		Per cent.
11-12	192·3-192·9	291-292	139·1-143·8

POPPY SEED OIL

French—*Huile d'œillette, Huile de pavot.* German—*Mohnoel.*
Italian—*Olio di papavero.*

For table of constants see pp. 486, 487.

Poppy seed oil is obtained from the seeds of the poppy, *Papaver somniferum*, by pressing. The plant is grown extensively in Asia Minor, Persia, India, Egypt, and South Russia; the seeds yield from 45-50 per cent of oil. The "cold-drawn" oil, the oil of the first pressing, is almost colourless or very pale golden yellow; this is the "white poppy seed oil" of commerce. The second quality, expressed at a higher temperature, is much inferior, and constitutes the "red poppy seed oil" of commerce.

Poppy seed oil has little or no odour and a pleasant taste, so that it is largely used as salad oil, especially as it does not easily turn rancid. The oil of unsound quality, however, possesses an acrid taste.

In the following table the acid values of a number of commercial samples are recorded:—

Kind of Oil.	Free Fatty Acids calculated to Oleic Acid.	Observer.
	Per cent.	
	2·09	Rechenberg
	2·29	Salkowski
Salad oil, 26 samples	0·70-2·86	Nördlinger
Commercial oil, expressed, 5 samples	12·87-17·73	,,
Commercial oil, extracted, 5 samples	2·15-9·43	,,
East Indian oils, expressed, 4 samples	3·2-5·5	Crossley and Le Sueur[1]

The solid fatty acids in poppy seed oil have not yet been investigated; according to older statements, lauric and myristic acids are

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[1] *Journ. Soc. Chem. Ind.* 1898, 991.

absent, whilst palmitic and stearic acids are said to be present. It is, however, most likely that palmitic acid is the only solid acid. According to *Tolman* and *Munson*[1] the proportion of solid fatty acids, as determined by the lead-salt-ether method, is 6·67 per cent of the total fatty acids. The liquid fatty acids in poppy seed oil were stated by *Hazura* and *Grüssner* to consist of 5 per cent of linolenic acid, 65 per cent of linolic acid, and about 30 per cent of oleic acid. Since, however, the liquid fatty acids from poppy seed oil yield practically no hexabromides, the quantity of linolenic acid must be very small. According to a recent examination, by *Utz*,[2] of poppy seed oils, obtained by extracting the seed with petroleum ether, the iodine value lies much higher than has been found hitherto. In the following table I reproduce *Utz's* results :—

	Iodine Value.	Refractive Index. At 15° C.	Butyro-refractometer. "Degrees" at 15° C.
Indian poppy seed oil	153·48	1·4772	78·1
Levantine ,, ,,	157·52	1·4774	78·4
German ,, ,,	156·94	1·4774	78·4

The unsaponifiable matter in poppy seed oil amounts to about 0·5 per cent, and consists chiefly of phytosterol, with which is admixed some impurity that can only be separated from the phytosterol by repeated crystallisation. Thus the crude phytosterol had to be recrystallised eight times before crystals of the melting point 136-137° C. could be obtained. The crystals of phytosteryl acetate from poppy seed oil melted at 125·5-126° C. (*Bömer* and *Winter*).

Poppy seed oil is, as a rule, contaminated with small quantities of sesamé oil, owing to the seed being usually expressed in the same works where sesamé oil is produced. Edible poppy seed oil is at present frequently adulterated with sesamé oil[2] and also with hazelnut oil, to improve the taste of edible oil obtained from stored seed. Both adulterants are detected by the lower iodine absorption of the sample; the presence of sesamé oil is ascertained by the characteristic *Baudouin* colour reaction (cp. "Sesamé Oil," p. 542).

The differentiation of poppy seed oil from walnut oil is of importance in the examination of white paints. The readiest means for this purpose is furnished by the hexabromide test; walnut oil yields from 1·4 to 1·9 per cent of hexabrominated glycerides, whereas poppy seed oil yields none.

Poppy seed oil is in its turn fraudulently added to olive oil (cp. p. 629); the high iodine value (unless masked by the addition of lard oil), in conjunction with a comparatively high specific gravity, indicate the adulteration.

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[1] *Journ. Amer. Chem. Soc.* 1903, 690.

[2] *Chemiker Zeitung*, 1903, 1177; 1904, 257.

Physical and Chemical Constants of Poppy Seed Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.	
At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
15	0·924	Souchère	−18	Girard	194·6	Valenta	136	Hübl
"	0·924-0·927	Allen			192·8	Moore	134	Moore
"	0·9262	Clarke			197·7	Dieterich	137·6-143·3	Dieterich
"	0·924	Massie			193·6	De Negri and Fabris	139-141	Peters
"	0·927	De Negri and Fabris			192-195	Oliveri	134-135	Souchère
15·5 (water at 15·5=1)	0·9255-0·9268[2]	Crossley and Le Sueur			190·1	Lewkowitsch	136·8-137·6	De Negri and Fabris
18	0·9245	Stilurell			193-194	Thoerner	133-138	Oliveri
98·99 (water at 15·5=1)	0·8738	Allen			189·0 196·8[2]	Crossley and Le Sueur	132·6-136	Lewkowitsch
							134-135	Thoerner
							133·7-137·1[2]	Crossley and Le Sueur
							153·8-157·5	Utz

Reichert-Meissl Value.		Hehner Value.		Maumené Test.		Viscosity.	
c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.	Seconds at 70° F.	Observer.
0·00[2]	Crossley and Le Sueur	95·38	Dietzell and Kressner	86-88	Archbutt	253·9 259·1	Crossley and Le Sueur
		94·97[2]	Crossley and Le Sueur	87-88·5	De Negri and Fabris		

Refractive Index.

At 0° C.		Observer.
15	1·4773	Utz
60	1·4586	Thoerner

Oleo-refractometer.

"Degrees."	Observer.
+23·5 to +29 +35[1]	Jean
+30 to +35 at 22° C.	Pearmain

Butyro-refractometer.

At °C.		Observer.
15	78·3	Utz
25	74·5	Mansfeld
	72	Beckurts and Seiler
40	63·4[2]	Crossley and Le Sueur

---

[1] Very old sample.

[2] East Indian oils from the Punjab, Bengal, and the N.W. Provinces.

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.		Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.		Refractive Index.	
At 100° C. Water at 100° = 1.	Observer.	°C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	At 60° C.	Observer.
0·8886	Archbutt	16·5	Hübl	20·5	Hübl	199	Thoerner	139	De Negri and Fabris	1·4506	Thoerner
		16·5	Thoerner	20-21	De Negri and Fabris						
				20·5	Thoerner			116·3	Thoerner		
		Titer Test.						Liquid Fatty Acids.			
		15·4-16·2	Lewkowitsch					149·6	Tortelli and Ruggeri		

The finer qualities of oil are used for edible purposes, and also for the best paints for artists. A mixture of equal volumes of "sun-bleached" poppy seed oil and bleached poppy seed oil varnish is extensively used for white pigments (*Lotter*[1]). A solution of fused gum mastic and Japan wax in poppy seed oil is obtainable in commerce as "wax oil." On account of the high price of poppy seed oil only the lowest qualities can be employed for making soft soaps.

AMOORA OIL

Physical and Chemical Constants of Amoora Oil

Specific Gravity.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Hehner Value.	Refractive Index.	Viscosity.
At 15° C. (water at 15·5 = 1).	Mgrms. KOH.	Per cent.	cc. $\frac{1}{10}$ norm. KOH.	Per cent.	Butyro-refractometer. At 40° C.	Number of Seconds. At 70° F.
0·9386	189·7	134·86	1·64	93·23	64·5	375·8

This oil is expressed in Bengal from the seeds of *Amoora Rohituka* (Evergreen tree) as a clear, reddish-brown oil, having a slight odour, resembling that of linseed oil. The specimen examined by *Crossley* and *Le Sueur*[2] had the acid value 17·03.

The oil is used by the natives medicinally and also as a burning oil.

ASPARAGUS SEED OIL[3]

French—*Huile d'asperges.* German—*Spargelsamenoel.*

Asparagus seed contains 15·3 per cent of a fatty oil of yellowish colour.

Specific Gravity at 15° C.	Saponification Value.	Iodine Value.	Butyro-refractometer. "Degrees" at 25° C.
0·928	194·1	137·1	75

The oil dries on exposure to the atmosphere, in a thin layer, to a hard, varnish-like mass.

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[1] *Journ. Soc. Chem. Ind.* 1895, 168.

[2] *Ibid.* 1898, 991.

[3] W. Peters, *Archiv der Pharmacie*, 1902, 53.

The glycerides in asparagus seed oil consist of palmitin, stearin, olein, and linolin. The presence of olein and linolin was proved by oxidising the liquid fatty acids, when dihydroxystearic acid and sativic acid were obtained. It is very likely that also linolenin and isolinolenin occur in the oil.

NIGER SEED OIL

French—*Huile de Niger.* German—*Nigeroel.*
Italian—*Olio di Niger.*

For tables of constants see p. 490.

Niger seed oil is expressed from the seeds of *Guizotia oleifera*, a plant cultivated in the East and West Indies; it is also grown in Germany. The oil is yellow and has a nutty taste. Four specimens of East Indian oils examined by *Crossley* and *Le Sueur*[1] had acid values ranging from 5·21 to 11·69; three samples were optically inactive, whereas the fourth deviated the plane of polarisation slightly to the right, viz. + 0° 18′.

Niger seed is crushed in this country (Hull); the oil is used as a substitute for linseed oil, and for adulterating rape oil.

---

[1] *Journ. Soc. Chem. Ind.* 1898, 991.

[Table

Physical and Chemical Constants of Niger Seed Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Hehner Value.		Maumene Test.		Refractive Index.		Viscosity.	
															Oleo-refractometer.			
At ° C.		Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	cc. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	° C.	Observer.	"Degrees."	Observer.	Seconds at 70° F.	Observer.
15·5 (water at 15·5=1)	0·9270 0·9248-0·9263	Allen Crossley and	-9	Allen	189-191 188·9-192·2	Stoddard Crossley and Le Sueur[1]	132·9 133·5 126·6-133·8	Archbutt Wallenstein and Finck Crossley and Le Sueur	0·11-0·63	Crossley and Le Sueur[1]	94·11	Crossley and Le Sueur[1]	82 81	Baynes Allen	+26 to +30 at 22° C.	Pearmain	263·1-292·6	Crossley and Le Sueur
99 (water at 15·5=1)	0·8738	Le Sueur[1]													Butyro-refractometer.			
															63·0 at 40° C.	Crossley and Le Sueur		

[1] East Indian Oils (*Journ. Soc. Chem. Ind.* 1898, 991).

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.		Iodine Value of the Liquid Fatty Acids.	
At 100° C. (water at 100=1).	Observer.	Per cent.	Observer.
0·8886	Archbutt	147·5	Wallenstein and Finck.

SUNFLOWER OIL

French—*Huile de tournesol.* German—*Sonnenblumenoel.*
Italian—*Olio dio girasole.*

For tables of constants see p. 492.

This oil, obtained from the seeds of *Helianthus annuus,* is a pale yellow oil of mild taste and pleasant smell. The sunflower plant is largely cultivated for oil-yielding purposes in Russia, Hungary, India, and China. The Hungarian[1] kernels are richer in oil than the Russian. The Hungarian seeds consist of 45-52 per cent of kernels, and 45-55 per cent of husks. The kernels contain 36·6 to 53 per cent of oil. On a practical scale 28-30 per cent of oil are recovered. The Russian seeds yield 23 per cent of oil only.

Attempts made in the United States to grow the plant for commercial purposes (to prepare edible oil) have not proved satisfactory; the cultivation of the plant has therefore been abandoned.

Sunflower oil contains from 0·31 to 0·72 per cent of unsaponifiable matter; a specimen prepared by *Holde*[2] from sunflower seed by extraction with petroleum ether contained 5·6 per cent of free fatty acids (calculated to oleic acid). The liquid fatty acids consist chiefly of linolic acid, oleic acid being present in small quantities only.

This oil dries more slowly than those already described. The absorption of oxygen, according to *Hübl's* method, using copper powder as an oxygen carrier, took place at the following rate:—

Absorption of Oxygen.	After 2 days.	After 7 days.	After 30 days.
	Per cent.	Per cent.	Per cent.
Sunflower oil	1·97	5·02	...
Sunflower oil fatty acids	0·85	3·56	6·3

The sunflower is chiefly cultivated in Southern Russia,[3] where the "cold drawn" oil serves for culinary purposes; the hot expressed oil is employed in soap-making and for the manufacture of varnishes. It is also used in Russia in the manufacture of margarine (*Jolles*[4]).

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[1] R. Windisch, *Landw. Versuchs-Stat.* 1902, 305.

[2] *Journ. Soc. Chem. Ind.* 1894, 892.

[3] *Ibid.* 1892, 470.

[4] *Ibid.* 1893, 935.

[TABLE

Physical and Chemical Constants of Sunflower Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Hehner Value.		Maumené Test.		Refractive Index.	
At ° C.		Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	Per cent.	Observer.	° C.	Observer.	At 60° C.	Observer.
15	0·924-0·926	Allen	-16 to -18·5	Bornemann	193-194	Bornemann	129	Spüller	95	Spüller	72-75	De Negri and Fabris	1·4611	Thoerner
,,	0·926	De Negri and Fabris			193-193·3	Spüller	122·5-133·3	Dieterich			67·5	Spüller	Oleo-refractometer.	
,,	0·936	Dieterich	at -17 partially solid	Holde	188-189	De Negri and Fabris	119·7-120·2	De Negri and Fabris					“ Degrees.”	Observer.
,,	0·9240	Holde			193	Holde	135	Holde					+35 at 22° C.	Pearmain
90	0·919	,,			193-194	Thoerner	129	Thoerner					Butyro-refractometer.	
													At 25° C.	Observer.
													72·2	Beckurts and Seiler

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.		Refractive Index.	
° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	At 60° C.	Observer.
17	Bach	23	Bach	201·5	Spüller	133·2-134	Spüller	1·4531	Thoerner
18	Dieterich	23	Dieterich	201·6	Thoerner	124 124	De Negri and Fabris		
18	De Negri and Fabris	17-22	Peters			133-134	Thoerner		
		22-24	De Negri and Fabris						
17	Thoerner	23	Thoerner						

YELLOW-ACACIA OIL [1]

German—*Gelb-Akazienoel.*

This oil is obtained from the seeds of the yellow acacia, *Caragena arborescens*, largely cultivated in South Russia. The seeds yield 12·4 per cent of oil on extraction with petroleum ether. The unsaponifiable matter in the oil amounted to only 0·14 per cent.

Physical and Chemical Constants of Yellow Acacia Oil

Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Hehner Value.
190·6	128·9	2·7	93·94

Physical and Chemical Constants of the Mixed Fatty Acids

Neutralisation Number.	Mean Molecular Weight.	Iodine Value.
199·0	280·9	131·7

By means of the lead-salt-ether method 8·74 per cent of solid fatty acids were found. Amongst these were identified palmitic, stearic, and erucic acids. The liquid fatty acids consisted of oleic and linolic acids. The less pronounced drying power of this oil, as compared with white acacia oil, is explained by the absence of linolenic acid.

PARA RUBBER TREE SEED OIL [2]

French—*Huile de siphonie élastique.* German—*Parakautschukbaumoel.*
Italian—*Olio (d'albero) di cacciù.*

This oil has been obtained from the kernels of the para rubber tree (*Hevea brasiliensis*). The seeds contained about 50 per cent of kernels. On extracting with petroleum ether, the kernels yielded 42·3 per cent of oil.

---

[1] Valentin Jones, *Mittheil. d. k. k. technolog. Gewerbe-Museums*, 1903, 223.

[2] *Bull. Imper. Inst.* 1903, 156.

The oil is of a light yellow colour, and has an odour resembling that of linseed oil. When exposed to the atmosphere it dries to a clear transparent film.

Physical and Chemical Constants of Para Rubber Tree Seed Oil

Specific Gravity. At 15° C.	Saponification Value.	Iodine Value.
0·9302	206·1	128·3

The specimen examined contained 5·4 per cent of free fatty acids.

ARGEMONE OIL[1]

French—*Huile de Pavot Épineux.* German—*Argemoneoel.*
Italian—*Olio di Argemona.*

Physical and Chemical Constants of Argemone Oil

Specific Gravity.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Hehner Value.	Refractive Index. At 40° C.	Viscosity in Redwood's Viscosimeter.
At 15·5° (water 15·5=1).	Mgrms. KOH.	Per cent.	c.c. $\frac{1}{10}$ Norm. KOH.	Per cent.	Butyro-refractometer.	Number of Seconds at 70° F.
0·9247-0·9259	187·8-190·3	119·91-122·5	0·00	95·07	62·5	268·9-272

Argemone oil is expressed from the seeds of *Argemone Mexicana*, Linn. the Mexican or prickly poppy. The fresh oil is of orange colour, and has a slight, but distinctive smell.

Volatile acids—acetic, butyric, and valeric, stated to occur in Argemone oil—could not be detected in the two genuine specimens examined by *Crossley* and *Le Sueur*. These specimens had the acid values 6·0 and 83·9 respectively. Hence the second specimen was completely soluble in 9 to 10 volumes of absolute alcohol at the ordinary temperature.

Argemone oil is used as an edible oil in the East Indies, where it can be obtained in practically unlimited quantities. In the West Indies and in Mexico the oil is used as a lubricant and illuminant.

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[1] Crossley and Le Sueur, *Journ. Soc. Chem. Ind.* 1898, 991.

FIR SEED OIL

French—*Huile de Pignon.* German—*Fichtensamenoel.*
Italian—*Olio di pinoli.*

For tables of constants see p. 496.

Fir seed oil is obtained from the seeds of several kinds of pine-trees—*Pinus sylvestris* (Scotch fir seed), *Pinus picea* and *Pinus abies.*[1]

This oil is of pale yellow colour (Scotch fir seed oil brownish yellow—*Allen*), and has a sweet taste.

Fir seed oils dry easily, and are therefore used in the preparation of varnishes.

The following are the constants of the oils obtained from the different seeds :—

---

[1] The fatty oil from *Pinus Monophylla* (?) is described as *Pine nut oil* by Blasdale (*Journ. Soc. Chem. Ind.* 1896, 205). It is a brown, drying oil with an unpleasant odour and taste. The following constants are given :—

Physical and Chemical Constants of Pine Nut Oil.

Spec. Grav. at 15° C.	Saponification Value.	Iodine Value.	Maumené Test.	Refractive Index.
0·933	192·8	101·3	71°	1·4769

Physical and Chemical Constants of the Mixed Fatty Acids.

Melting point	19° C.

[TABLE

Physical and Chemical Constants of Fir Seed Oil

Source.	Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.	
	At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.
Pinus sylvestris	15	0·9312	De Fontenelle	– 27 to – 30	De Fontenelle						
Pinus abies .	,,	0·9285	,,								
Pinus picea .	,,	0·9215	De Negri and Fabris	– 18 to – 20	De Negri and Fabris	191·3	De Negri and Fabris	118·9-120	De Negri and Fabris	98-99	De Negri and Fabris

Physical and Chemical Constants of the Mixed Fatty Acids

Source.	Solidifying Point.		Melting Point.		Iodine Value.	
	°C.	Observer.	°C.	Observer.	Per cent.	Observer.
Pinus picea, expressed . . .	10-15	De Negri and Fabris	16-19	De Negri and Fabris	121·5	De Negri and Fabris
,, ,, extracted . . .	12-16	,,	17-19	,,		

MADIA OIL

French—*Huile de Madia.* German—*Madiaoel.*
Italian—*Olio di Madia.*

For tables of constants see p. 498.

Madia oil is obtained from the seeds of the Chilian plant *Madia sativa*, which has been also cultivated successfully in South Germany. The seeds contain 32-33 per cent of oil. This oil is dark yellow, and has a characteristic, not unpleasant odour.

Madia oil occupies an intermediate place between drying and semi-drying oils. Treated with nitrous acid (elaïdin test) it remains liquid; for this reason, as also on account of its high iodine value, I have placed it amongst the drying oils. It absorbs, indeed, considerable quantities of oxygen, thereby becoming viscid.

The oil is chiefly used for burning; it is also used for soap-making.

[TABLE

Physical and Chemical Constants of Madia Oil

Specific Gravity.		Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.	
At 15° C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.
0·926-0·928	Hartwich	– 10 to – 17 (by hot pressure)	Winkler	192·8	De Negri and Fabris	117·5-119·5	De Negri and Fabris	95-99	De Negri and Fabris
0·9285	De Negri and Fabris	– 22·5 (cold-drawn)	Riegler						
0·9286	Winkler	– 12 to – 15	De Negri and Fabris						

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.
20-22	De Negri and Fabris	23-26	De Negri and Fabris	120·7	De Negri and Fabris

Lesser Known Drying Oils

STRAWBERRY SEED OIL

French—*Huile de fraises.* German—*Erdbeerenoel.*
Italian—*Olio di fragola.*

The strawberry seeds contain 19·02 per cent of this oil (*Anarin*[1]). The oil is stated to dry as quickly as linseed oil. The iodine value of the insoluble fatty acids is 191-193.

Physical and Chemical Constants of Strawberry Seed Oil

Specific Gravity. At 15° C.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.
0·9345	193·7	180·3	2·1

ISANO (UNGUEKO) OIL[2]

Isano (I'Sano) oil is obtained from the seeds of the I'Sano[3] or Ungueko,[4] a large tree of the family *Oleaceæ*, growing in the French Congo. The ground and dried seeds yield 60 per cent of oil.

The specific gravity of the oil is 0·973 at 23° C. It is liquid even at – 15° C., is reddish in colour, has an insipid flavour and fishy smell. The oil is viscous and possesses strong drying powers. Tested by *Maumené's* test it gives a thermal reaction of 115° C. The bromine value is stated to be double that of oleic acid. It is further stated that the oil contains 86 per cent of liquid fatty acids (the lead salts being entirely soluble in ether), consisting of 15 per cent oleic acid, 75 per cent linolic acid, and 10 per cent of isanic acid (chap. iii. p. 115). On saponification from 12 to 13 per cent of glycerol are said to be obtained.

MOHAMBA OIL[2]

The seeds yielding Mohamba oil are very similar to those of the Isano tree, but after drying they give only 12 per cent of oil.

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[1] Prot. *Russ. Phys. Chem. Soc.* 1903, 213.

[2] Hébert, *Journ. Soc. Chem. Ind.* 1896, 660.

[3] Local name in Loango.

[4] Local name.

The oil has the specific gravity of 0·915 at 23° C.; it remains liquid at −15° C., is of yellow colour, fairly fluid, inodorous, and of insipid taste. In *Maumené's* test the oil gave a rise of 55° C.

On saponification about 9 per cent of glycerol and 90 per cent of brown liquid unsaturated fatty acids are obtained from the oil. From the lead salts of the acids, which are entirely soluble in ether, there was obtained, on separating the free acids, a white fatty acid, soluble in alcohol and ether, and crystallising from the latter in laminæ, melting at 34°-35° C. This acid absorbs about as much bromine as oleic acid, and would therefore belong to the oleic series, but does not seem to be identical with any known acid. The liquid acids appear to consist of oleic acid, as they absorb an amount of bromine corresponding to oleic acid and give the elaïdin reaction.

GARDEN ROCKET OIL[1]—DAME'S VIOLET OIL

French—*Huile de julienne.* German—*Rothrepsoel.*
Italian—*Olio di Hesperide.*

For tables of constants see p. 501.

This oil is expressed from the seeds of the garden rocket, *Hesperis matronalis.* When fresh it is of green colour, becoming brownish on keeping. It is an odourless oil possessing a somewhat bitter taste.

Garden rocket oil is expressed in France and Switzerland, and used as a burning oil.

---

[1] De Negri and Fabris, *Annali del Laborat. Chim. delle Gabelle*, 1891-92, 151.

[TABLE

Physical and Chemical Constants of Garden Rocket Oil

Specific Gravity.		Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.	
At 15° C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.
0·9282	Schübler	− 22 to − 23	Schaedler	191·8	De Negri and Fabris	154·9-155·3	De Negri and Fabris	125-127·5	De Negri and Fabris
0·9315	Villon								
0·9335	De Negri and Fabris								

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.	Melting Point.	Iodine Value.	Observer.
°C.	°C.	Per cent.	
16-14	20-22	157	De Negri and Fabris

HENBANE SEED OIL[1]

French—*Huile de jusquiame.* German—*Bilsenkrautsamenoel.*
Italian—*Olio di henbane.*

Henbane seed oil is obtained from the seeds of *Hyoscyamus niger.* This oil is yellow, somewhat viscous, slightly fluorescent, and dries readily.

Physical and Chemical Constants of Henbane Seed Oil

Spec. Gravity at 15° C.	Saponific. Value.	Iodine Value.	Reichert Value.	Hehner Value
0·939	170·8	138	0·99	94·7

CELOSIA OIL[2]

French—*Huile de Celosia.* German—*Celosiaoel.*
Italian—*Olio di celosia.*

This oil is obtained from the seeds of *Celosia cristata*, a plant indigenous in the East Indies and China; it is a greenish-brown drying oil.

Physical and Chemical Constants of Celosia Oil

Solidifying Point.	Saponific. Value.	Iodine Value.
−10° C.	190·5	126·3

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.	Melting Point.
21°-19° C.	27°-29° C.

INDIAN LAUREL OIL[3]

French—*Huile de laurier indien.* German—*Indisches Lerbeeroel.*
Italian—*Olio di lauro indico.*

The fruits from *Laurus indica* yield a brown, viscous oil, having the constants given in the following table. The specimen examined contained 33 per cent of free fatty acids.

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[1] Mjoen, *Journ. Soc. Chem. Ind.* 1897, 340.

[2] De Negri and Fabris, *Chem. Zeit.* 1896, Rep. 161.

[3] *Ibid.*

Physical and Chemical Constants of Indian Laurel Oil

Spec. Grav. at 15° C.	Solidifying Point.	Saponific. Value.	Iodine Value.
0·926	Thickens at – 15° C., but does not solidify.	170	118·6

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.	Melting Point.
19°-18° C.	24°-26° C.

TOBACCO SEED OIL

French—*Huile de Tabac.* German—*Tabaksamenoel.*
Italian—*Olio di tabacco.*

The oil has the specific gravity 0·9232 at 15° C. (*Schübler*), it solidifies at – 25° C. The colour of the oil is pale greenish-yellow. Tobacco seed oil dries readily.

WELD SEED OIL

German—*Resedasamenoel, Wausamenoel.*

This oil is obtained from the seeds of the dyer's weld, *Reseda luteola.* Owing to the presence of chlorophyll the oil has a dark greenish tint. Its specific gravity is 0·9358 (*Schübler*); its solidifying point – 20° C. It has a bitter taste and nauseous odour. The oil dries easily on exposure to air. It is used for burning and making varnishes.

(2) SEMI-DRYING OILS

The oils comprising this class form an intermediate link between the drying and the non-drying oils; this is readily expressed by their iodine values, which lie between those of the drying oils and the non-drying oils.

Chemically they differ from the drying oils by the absence of linolenic acids, whilst they are differentiated from the non-drying oils by the linolic acid they contain. The proportion of linolic acid decreases as the iodine values decrease. The members of this class appear to range themselves naturally into two groups:—

(α) Cotton Seed Oil Group.
(β) Rape Oil Group.

(α) *The Cotton Seed Oil Group*

The members of this group still possess distinct drying properties, although they are less pronounced than in the case of the true drying oils.

The drying power becomes more apparent on allowing the oils to dry at a somewhat elevated temperature. But even at the ordinary temperature maize oil and cotton oil form a viscous mass after exposure to the atmosphere for several weeks in thin layers. This group takes its name from its most prominent member, which may be considered as the type of a semi-drying oil; it contains a notable amount of linolic acid.

CAMELINE OIL (GERMAN SESAMÉ OIL)

French—*Huile de Cameline.* German—*Deutsches Sesamoel, Leindotteroel, Rülloel.* Italian—*Olio di cameline.*

For tables of constants see p. 505.

Cameline oil is obtained from the seeds of *Myagrum sativum* (or *Camelina sativa*), belonging to the *Cruciferæ.* The seeds contain 31-34 per cent of oil.

The oil has a golden-yellow colour and a pungent taste and smell.

On exposure to air it dries slowly. Boiled with litharge or manganese borate it yields a slowly drying varnish.

The low saponification value of the oil points to the presence of glycerides of erucic acid. The oil prepared by expression is free from sulphur, like all the oils drawn in the cold from seeds of the *Cruciferæ* (cp. "Rape Oil," p. 553).

On account of its low price the oil is not likely to be adulterated. It is used, however, for the adulteration of rape oil, in which it may be detected by its higher iodine value. Cameline oil is naturally present in linseed oil expressed from East Indian seed (cp. p. 449).

The cold drawn oil is sometimes employed for edible purposes. Its chief use, however, is for soap-making. It suitably replaces linseed oil during the winter in soft soap-making. In summer, however, cameline oil cannot be used alone, its potash soap being liquid at a temperature below 20° C.

Physical and Chemical Constants of Cameline Oil

Specific Gravity.		Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.		Refractive Index. Oleo-refractometer.	
At 15° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	° C.	Observer.	"Degrees" at 22° C.	Observer.
0·9260	Christiani	−18	Chateau	188	De Negri and Fabris	135·3	De Negri and Fabris	117	De Negri and Fabris	+32	Jean
0·9259	Massie					142·4	Tortelli and Ruggeri	82	Jean		
0·9252	Schübler										
0·9260	De Negri and Fabris										
0·9200	Levallois										
0·9240	Jean										

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.	
° C.	Observer.	° C.	Observer.	Per cent.	Observer.
14-13	De Negri and Fabris	18-20	De Negri and Fabris	136·8	De Negri and Fabris
				Iodine Value of Liquid Fatty Acids.	
				165·4	Tortelli and Ruggeri

CLOVER OIL (RED CLOVER OIL; WHITE CLOVER OIL)

French—*Huile de trèfle.* German—*Kleesamenoel.*
Italian—*Olio di trifoglio.*

This oil is obtained from the seeds of the clover, *Trifolium.* Two species of clover seed, viz. *Trifolium pratense perenne,* red clover, and *Trifolium repens,* white clover, were examined by *Valentin Jones.*[1] The seeds of the red clover yielded 11·1 per cent, and the seeds of the white clover 11·8 per cent of oil on extraction with petroleum ether.

Physical and Chemical Constants of Clover Oil

Clover Oil.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Hehner Value.
Red	189·9	124·3	3·3	93·62
White	189·5	119·7	3·5	93·24

Physical and Chemical Constants of the Mixed Fatty Acids

	Neutralisation Value.	Mean Molecular Weight.	Iodine Value.
Red	198·1	283·2	126·2
White	197·6	283·8	122·2

The solid fatty acids of red clover oil consist of palmitic and stearic acids. The liquid fatty acids contain oleic and linolic acids, the former predominating.

The white clover oil simulates very closely in its chemical composition the red clover oil. The lower iodine value points to a smaller proportion of liquid fatty acids in white clover oil.

SOJA BEAN OIL (SOY-BEAN OIL, BEAN OIL, CHINESE BEAN OIL)

French—*Huile de Soya.* German—*Saubohnenfelt, Sojabohnenoel.*
Italian—*Olio di Soia.*

For tables of constants see p. 508.

This oil is obtained from the seeds of *Soja hispida,* a plant indigenous in China, Manchuria, and Japan, where the oil is used for

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[1] *Mitth. d. k. k. Technolog. Gewerbe Museums,* 1903, 223.

edible purposes. The seeds contain 18 per cent of oil. The manufacture of soja bean oil forms one of the staple industries of Manchuria.[1] The plant is also extensively cultivated in Japan.[2] The beans contain besides the oil about 30-40 per cent of casein.[3]

A sample of the oil extracted with ether by *Morawski* and *Stingl* gave 0·22 per cent of unsaponifiable matter, and 2·28 per cent of free acid calculated to oleic acid.

The proportion of solid fatty acids in the oil is approximately 11·5 per cent of the total mixed fatty acids; *Lane* found 80·26 per cent of liquid fatty acids. The bulk of the solid fatty acids is stated to consist of palmitic acid; the liquid fatty acids consist of oleic and linolic acids.

On exposure to air it dries slowly with formation of a thin skin.

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[1] A. Hosie, *Manchuria*, Methuen and Co., London, 1901. Cp. also *Journ. Soc. Chem. Ind.* 1901, 642.

[2] Pozzi-Escot, *Revue gen. de chim. pur. et appl.* 1902, 64.

[3] O. Nagel, *Journ. Soc. Chem. Ind.* 1903, 1337.

Physical and Chemical Constants of Soja Bean Oil

Specific Gravity.		Solidifying Point.		Saponification Value.		Iodine Value.		Hehner Value.		Maumené Test.	
At 15° C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	Per cent.	Observer.	°C.	Observer.
0·9270	Morawski and Stingl	+15 to +8	De Negri and Fabris	192·9	Morawski and Stingl	122·2	Morawski and Stingl	95·5	Morawski and Stingl	61	Morawski and Stingl
0·9242	De Negri and Fabris			192·5	De Negri and Fabris	121·3	De Negri and Fabris			59	De Negri and Fabris
0·924	Shukoff[1]			190·6	Shukoff	124	Shukoff				

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.
25	Morawski and Stingl	28	Morawski and Stingl	115·2	Morawski and Stingl
25-23	De Negri and Fabris	27-29	De Negri and Fabris	122	De Negri and Fabris
24·1	Shukoff				
				Liquid Fatty Acids.	
				131	Lane

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[1] From seed grown in an experimental station in South Russia.

PUMPKIN SEED OIL

French—*Huile de courge.* German—*Kürbissamenoel, Kürbiskernoel.*
Italian—*Olio di zucca.*

For tables of constants see p. 510.

Pumpkin seed oil is obtained from the seeds of *Cucurbita pepo* by cold expression. In South Russia the oil is prepared on a commercial scale by roasting the seeds and subsequently expressing the oil in the hot.[1]

The seeds consist of 23·5 per cent husks and 76·5 per cent kernels ("meats"). The whole seeds contain from 35 to 37·5 per cent of oil; the kernels yield from 47 to 48 per cent of oil.

The oil obtained by cold expression has a greenish colour with a faint red fluorescence, whilst that prepared commercially, as described, is stated to be viscous and of a brownish green colour by transmitted light, and of a deep red colour in reflected light. It should be noted that the seeds are subjected to various degrees of drying and roasting, which no doubt exercise a considerable influence on the colour of the oil.

The constants obtained by *Poda* for oils prepared by himself by both methods agree closely with those yielded by commercial oils.

The oil has considerable drying properties. The cold-drawn oil is used for edible purposes (Austria, Hungary, Russia); it is stated that the oil from the large cucumber grown on the Slave Coast surpasses olive oil in flavour. The lower qualities of pumpkin seed oil serve as a burning oil.

Strauss[2] attempted to bleach the oil obtained by expressing the crushed seeds after heating them to 80°-90° C. with concentrated sulphuric acid, chlorine, ozone, and sulphurous acid, but the results were not satisfactory. Other experiments, having for their object the refining of the oil with caustic soda, yielded a pale oil, but the losses due to saponification were very considerable.

The edible oil is adulterated with linseed, cotton seed, sesamé, and rape oils. Linseed oil would be detected by its high iodine value and the hexabromide test; cotton seed oil by the *Halphen* colour reaction (see p. 530); sesamé oil by the *Baudouin* colour reaction (see p. 542); rape oil by a lower iodine value, in conjunction with a lower saponification value.

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[1] Poda, *Journ. Soc. Chem. Ind.* 1898, 1054.

[2] *Chem. Zeit.* 1903, 527.

Physical and Chemical Constants of Pumpkin Seed Oil

Specific Gravity.			Solidifyiug Point.		Saponification Value.		Iodine Value.		Hehner Value.		Refractive Index.	
At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer	Per cent.	Observer.	Per cent.	Observer.	Butyro-refractometer at 25° C.	Observer.
15	0·923-0·925	Poda [2]	–16	Schattenfroh	188·7	Schattenfroh	121	Hübl	96·2	Schattenfroh	70·2-72·5 [1]	Poda
15·5	0·9197	Graham [5]			188·4-190·2	Poda [2]	121·5	Henriques			70-72·5 [2]	,,
20	0·923	Schattenfroh					113·4	Schattenfroh				
							122·8-130·7	Poda [2]				
							120·5	Strauss				

Physical and Chemical Constants of the Mixed Fatty Acids

Melting Point.		Mean Molecular Weight.	
°C.	Observer.		Observer.
26·5-28·5 [3]	Poda	284·7	Schattenfroh
28·4-29·8 [4]	,,		

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[1] Mean values of cold-pressed and hot-pressed oil (*Journ. Soc. Chem. Ind.* 1898, 1054).

[2] Ten commercial oils.

[3] Point of incipient fusion.

[4] Point of complete fusion.

[5] *Amer. Journ. Pharm.* 1901, 352.

WATER-MELON OIL

French—*Huile de citrouille.* German—*Wassermelonenoel.*
Italian—*Olio di citriuolo.*

This oil is obtained from the kernels of *Cucumis citrullus*, ~~L.~~ Ser. (*Cucurbita citrullus* Lin.). The seeds yield 62 per cent kernels, which in their turn give 65·8 per cent of oil; hence the seeds contain 40·8 per cent of oil.

A specimen of oil examined by *Wijs*[1] contained 1·20 per cent free fatty acids; it gave the constants recorded in the table.

The oil neither gives the *Halphen* nor the *Baudouin* reaction.

Physical and Chemical Constants of Water-melon Oil

Specific Gravity.	Saponification Value.	Iodine Value.
At 20° C. (Water at 4° = 1).	Mgrms. KOH.	Per cent.
0·9160	189·7	118

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.	Melting Point.	Neutralisation Number.	Saponification Number.	Mean Molecular Weight.	Iodine Value.
°C.	°C.	Mgrms. KOH.	Mgrms. KOH.		Per cent.
Titer Test. 32	34	197·1	197·1	284·1	122·7

MELON SEED OIL[2]

French—*Huile des graines de melon.* German—*Melonenoel.*
Italian—*Oleo di mellone.*

Physical and Chemical Constants of Melon Seed Oil

Melting Point. °C.	Solidifying Point. °C.	Saponification Value.	Iodine Value.
5·5	5	193·3	101·5

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[1] *Zeits. f. Unters. d. Nahrungs. und Genussm.* 1903, 492.

[2] *Ibid.* 1903, 1025.

Physical and Chemical Constants of the Mixed Fatty Acids

Melting Point. °C.	Solidifying Point. °C.
39	36

Melon oil is obtained from the seeds of *Cucumis melo;* the seeds form an article of commerce on the Slave Coast and Gold Coast of West Africa. The seeds examined by *Fendler* contained 43·8 per cent of oil.

The specimen examined had the acid value 4·81.

MAIZE OIL, CORN OIL

French—*Huile de Maïs.* German—*Maisoel.* Italian—*Olio di Mais.*

For tables of constants see pp. 515-517.

This oil is obtained from the germs of the maize plant, *Zea Mays.* The germs are recovered in the process of manufacturing starch, by sifting and winnowing them from the starch granules, in which they are imbedded.

Formerly maize oil was obtained as a by-product in the alcohol distilleries. When the malted and crushed grain was allowed to ferment, the oil was laid bare and rose to the top in the fermentation vats. Before distilling off the alcohol the oil was ladled off and purified in a crude fashion by washing, filtering, and settling. Since, however, the presence of the germ not only imparts an unpleasant flavour to the spirit obtained by fermentation, and the oil so obtained was very impure, and had a different character from the oil expressed from the germs, the older process of fermenting the crushed grain has been abandoned, and the corn is now first malted and crushed, and the germ separated by sifting. At present, maize oil is manufactured on a very large scale from the isolated germs by pressure in hydraulic presses. The germs contain in a dry condition 53 per cent of oil and yield in practice about 40 per cent of oil. (The whole grain contains 6-10 per cent of oil.)

The freshly-prepared maize oil is of a pale yellow or golden yellow colour, and has a characteristic odour; its taste is pleasant at first, and is most characteristic in that it resembles that of newly ground cornmeal. It is therefore possible to identify the oil by its taste alone.

The freshly-prepared oil from the germs contains but small quantities of free fatty acids, whereas the oil recovered by the older processes from the fermentation vats is characterised by a large amount of free fatty acids. The solubilities of the oil in absolute alcohol, acetone, and glacial acetic acid, are collated in the following table, due to *Smith*:[1]—

Solubility of Maize Oil in 100 volumes of				
Absolute Alcohol.		Acetone, commercial.	Glacial Acetic Acid.	
At 16° C.	At 63° C.	At 16° C.	At 16° C.	At 63° C.
2	13	24	3	9

Maize oil is characterised by its high amount of unsaponifiable matter. *Spüller*[2] obtained 1·35 per cent, and *Hart*[3] 1·55 per cent, of unsaponifiable matter. *Hopkins* found in a specimen of maize oil 1·49 per cent of lecithin and 1·37 per cent of phytosterol (?). A sample of maize oil examined in my laboratory gave even 2·32 per cent of unsaponifiable matter.

The "unsaponifiable" consists of lecithin, and of an alcohol which was looked upon by earlier observers (*Hoppe-Seyler*, *Hopkins*) as cholesterol. Since, however, purified crystals obtained by *Gill* and *Tufts*[4] from about 4 kilos of maize oil melted at about 138-138·3° C., the alcohol appears to be phytosterol. The fact that the acetate melted at 127·1° C., and that it seemed to be less soluble in alcohol than the corresponding substance obtained from olive oil, led *Gill* and *Tufts* to the conclusion that the alcohol in the unsaponifiable matter of maize oil is sitosterol and not phytosterol (cp. p. 143).

In the elaïdin test, maize oil, like cotton seed oil, yields a mass of buttery or pasty consistence.

Maize oil is, as one would expect from its high iodine value,[5] a good type of a semi-drying oil; it is a rather more strongly drying oil than cotton seed oil, but it differs from cotton seed oil in that it does not oxidise with equal energy, when finely subdivided on cotton waste, although it heats with sufficient rapidity to render it dangerous as a lubricating oil (Chap. XV.). In the *Livache* test two samples of maize oil of different origin gained 5·97 and 5·19 per cent in seven and ten days respectively.[6]

The saturated fatty acids in maize oil amount, according to *Hopkins*, to 4·55 per cent; *Tolman* and *Munson*, however, obtained 7·44 per cent of solid fatty acids by the lead-salt-ether method. Hence, *Vulté* and *Gibson's* statement that the mixed fatty acids consist of 27·74 per cent solid fatty acids and 72·26 per cent liquid fatty acids, can only be explained by the fact that the solid acids

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[1] *Journ. Soc. Chem. Ind.* 1892, 505.

[2] *Dingl. Polyt. Journ.* 264, 626.

[3] *Journ. Soc. Chem. Ind.* 1894, 257.

[4] *Journ. Amer. Chem. Soc.* 1903, 251.

[5] *Rokitansky* (*Journ. Chem. Soc.* 1895, Abstr. i. 509) describes a maize oil obtained from the yellow Italian maize plant, grown in Southern Russia, as a yellow, neutral oil of 0·836 specific gravity, and the (Hübl) iodine number 75·8. These numbers differ so much from those given in the table, that they have not been embodied therein.

[6] H. Winfield, *Dissertation*, New York, 1899.

had not been completely exhausted with ether. This is confirmed by their further statement that the separated solid fatty acids still absorbed 54·23 per cent of iodine.

According to *Vulté* and *Gibson* the solid fatty acids consist of palmitic, stearic, and arachidic acids, but considering that *Hehner* and *Mitchell* found no stearic acid in maize oil, this statement stands in need of confirmation. Amongst the liquid fatty acids linolenic acid seems to be absent, since no hexabrominated glycerides could be obtained; nor did *Hopkins*[1] find any linusic acid amongst the products of oxidation. Since tetrabromostearic acid was obtained from the liquid fatty acids, the presence of linolic acid is proved. The liquid fatty acid may therefore be considered as consisting of a mixture of linolic and oleic acids. Small quantities of volatile fatty acids occur in the oil, as is evidenced by the high *Reichert* value. Amongst the volatile fatty acids, acetic and formic acids were identified. *Lewkowitsch* found the acetyl value of a sample of maize oil 7·8-8·75; this somewhat high value may be due to some extent at least to the high amount of unsaponifiable matter.

No decided drying properties are imparted to maize oil by subjecting it to the process of "boiling," or by the addition of driers. If, however, a current of air is passed through the oil at 150° C., it acquires on addition of manganese borate some drying properties, and a thin film of the oil so treated spread on lead dries in from ten to twenty hours to a viscous mass.

At times when cotton seed oil is lower in price than maize oil, the latter may be adulterated with cotton seed oil. Although it is easy to differentiate maize oil from cotton seed oil, the detection of a small proportion of maize oil in cotton seed oil is at present impossible by merely chemical tests. *Gill* and *Tufts* are of the opinion that it may be feasible to detect cotton seed oil in maize oil by the melting point of the acetate of the alcohol isolated from the unsaponifiable matter. They obtained from pure cotton seed oil, after recrystallising the acetate six times, crystals of the melting point 120-121° C., from a mixture of 90 per cent of cotton seed oil and 10 per cent of maize oil crystals melting at 121·5-122·5° C., and from a mixture of 80 per cent of cotton seed oil and 20 per cent of maize oil crystals melting at 124-125° C., whereas crystals from pure maize oil melted at 127·1° C. Since, however, *Bömer* and *Winter* obtained phytosteryl acetate from cotton seed oil of the melting point 123-124° C., further confirmation of the reliability of the "sitosterol test" is required. In the present state of our knowledge the *Halphen* colour test (in which maize oil remains unchanged) and a higher titer test of the fatty acids than 20° C., must be relied upon as indicating the presence of cotton seed oil.

In consequence of the enormous quantities of maize oil that are produced in the United States, and in view of the almost unlimited supply that can be obtained, it is rather to be expected that maize oil will in future be used to adulterate cotton seed oil.

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[1] *Journ. Amer. Chem. Soc.* 1899, 948.

Physical and Chemical Constants of Maize Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Reichert Value.	
At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.
15	0·9215	Bornemann	−10 to −20	Smith	188-189	Spüller	119·4-119·9	Spüller	0·33	Spüller
,,	0·9244	Smith	−10 to −15	De Negri and Fabris	193·4	Smith	116·3	Smetham	2·5[1]	Smith
,,	0·9215-0·9220	De Negri and Fabris			190·4	De Negri and Fabris	122·9	Smith	4·2-4·3	Winfield[2]
			−36	Hopkins			111·2-112·6	De Negri and Fabris		
,,	0·9239	Hart	"stearine" deposits at the ordinary temperature on standing	Lewkowitsch	189·7	Archbutt				
15·5	0·9274	Lewkowitsch			192·6	Winfield	117	Hart		
,,	0·9243	Archbutt			191·9	Lewkowitsch	121-130·8	Lewkowitsch		
,,	0·9213-0·9255	Winfield					122	Wallenstein		
							121·5-123·1	Hopkins		
100	0·8711-0·8756	,,					122·2-128·02	Williams		

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[1] The volatile acids from 108 grms. of oil required 0·56 grms. KOH (*Journ. Soc. Chem. Ind.* 1892, 505).

[2] One sample of "distillery oil" is stated to have as low a Hehner value as 88·21, and the correspondingly high Reichert value of 9·9.

Physical and Chemical Constants of Maize Oil—continued

Hehner Value.		Refractive Index.		Thermal Tests.			
				Maumené Test.		Heat of Bromination.	
Per cent.	Observer.	At 15·5° C.	Observer.	° C.	Observer.	° C.	Observer.
94·7	Spüller	1·4768	Tolman and Munson	56	Spüller[1]	21·5	Hehner and Mitchell
95·7	Hart			86	De Negri and Fabris[2]		
93·57	Hopkins	Butyro-refractometer.		89	Smith[3]		
92·2-92·8	Winfield	"Degrees" at 15° C.	Observer.	60·5	Hart[1]		
		77·5	Tolman and Munson	79	Jean[2]		
				81·6	Archbutt		

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[1] By Maumené's method, p. 314.

[2] By Jean's method, p. 318.

[3] 15 grms. of oil and 5 c.c. of sulphuric acid.

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.			Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.	
°C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
100	0·8529	Winfield	16-14	De Negri and Fabris	18-20	De Negri and Fabris	198·4	Spüller	125	Spüller
					20	Jean			113-115	De Negri and Fabris
					21·6	Tolman and Munson				
			Titer Test.						Iodine Value of the Liquid Fatty Acids.	
			19	Lewkowitsch					140·7	Wallenstein and Finck
									142·2-143·7[1]	Tortelli and Ruggeri

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[1] From an oil having the iodine value 123·3-124·6.

Well-refined maize oil is used as an edible oil (salad oil). Since its "grainy" taste is objectionable, the edible quality will most likely be mixed with edible cotton oil and other edible oils. Maize oil is also used in the manufacture of margarine—"oleo-margarine" of the United States—as also in the manufacture of compound lard in place of cotton seed oil. The chief use of such maize oil as cannot be employed for edible purposes is for making soft soap, for which it is eminently suitable. To indicate the extent to which maize oil has been employed in Europe for soap-making, the following numbers, showing the increase of exports from the United States during the years 1897 and 1900 as 2,646,560 to 4,389,929 gallons respectively, may be quoted. (It is noteworthy that in consequence of the lower prices of cotton oil ruling in the years 1902 and 1903, the import of maize oil into this country has at present almost ceased.) Lower qualities are used as a burning oil. The oil has also been recommended as a lubricating oil, but on account of its gumming properties it cannot be usefully employed for this purpose. Its viscosity has been stated by *Winfield* at 20° C. to be 9·79-10·7 times that of water. Taking the viscosity of rape oil at 100, the viscosity of maize oil works out at 70·4-70·65. Notwithstanding many statements to the contrary, maize oil cannot be used as a paint oil on account of the poor drying properties paints prepared with this oil possess.

DAPHNE OIL[1]

German—*Daphneoel.*

This oil is obtained from the seeds of *Daphne Gnidium* (*semen coccognidii*) and other Daphne species such as *D. Mezereum*. The seeds contain from 36-37 per cent of oil; the oil has a greenish yellow colour, and dries on exposure to the atmosphere.

The solid fatty acids of the oil consist of palmitic and stearic acids; the statement that the liquid fatty acids contain besides oleic and linolic acids also linolenic and isolinolenic acids requires confirmation.

Physical and Chemical Constants of Daphne Oil

Specific Gravity. At 15° C.	Saponification Value. Mgrms. KOH.	Iodine Value. Per cent.
0·9237	196·5	126·1

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[1] Peters, *Arch. d. Pharm.* 1902, 240.

WHEAT OIL

French—*Huile de blé.* German—*Weizenkernoel.*
Italian—*Olio di germi di grano.*

For tables of constants see p. 520.

Wheat oil is contained in the germs of the wheat grains to the extent of 12·5 per cent.

In the fresh state the oil is pale yellow and has the characteristic odour of wheat meal. It is insoluble in anhydrous alcohol in the cold, but dissolves in 30 parts of hot absolute alcohol. At 65° C. it is soluble in an equal volume of glacial acetic acid.

The oil easily turns rancid (most likely owing to the presence of a ferment; cp. "Rice Oil") and thereby becomes dark brown. A freshly extracted specimen contained 5·65 per cent free fatty acids calculated to oleic acid; after one year the same sample contained 43·86 per cent. Oils from different germs will behave differently, as shown by the numbers given in the tables.

The specimen examined by *Frankforter* and *Harding* contained 2 per cent of lecithin and 2·5 per cent of phytosterol. In the opinion of *Frankforter* and *Harding* the alcohol resembles *Reinke* and *Rodwald's* paracholesterol (sitosterol (?)). The high percentage of both lecithin and alcohol shows the relationship of this oil to maize oil. This oil is not identical with wheat meal oil (cp. p. 596).

[TABLE

Physical and Chemical Constants of Wheat Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Refractive Index.		
At ° C.		Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	At ° C.		Observer.
15	0·9245	De Negri[1]	15	De Negri	182·81	De Negri	115·17	De Negri	20	1·48325	Frankforter and Harding
,,	0·9292-0·9374	Frankforter and Harding[2]	Semi-solid at 0	Frankforter and Harding	187·4-190·3	Frankforter and Harding	115·64	Frankforter and Harding	30	1·47936	
									40	1·47447	
									Butyro-refractometer.		
										74·5	De Negri

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[1] *Journ. Soc. Chem. Ind.* 1898, 1155.

[2] *Ibid.* 1899, 1030.

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.
29·7	De Negri	39·5	De Negri	123·27	De Negri

DATURA OIL[1]

French—*Huile de datura.* German—*Stechapfeloel, Daturaoel.*
Italian—*Olio di Stramonio.*

The air-dried seeds of *Datura Stramonium* (thorn apple) contain 16·7 per cent of datura oil.

The solid fatty acids of datura oil include amongst others:—daturic acid, palmitic acid, and an acid melting at 53°-54° C., and having a molecular weight exceeding 286. There appears to be present in the oil also a solid unsaturated acid which is stated to be readily oxidisable.

When heated to 50° C. in a thin layer for thirteen hours, the oil forms a firm skin; at the ordinary temperature it only begins to show signs of drying after 35 days.

The viscosity of the oil is 9 compared with water at 20° C.

Physical and Chemical Constants of Datura Oil

Specific Gravity at 15° C.	Solidifying Point.	Saponification Value. Mgrms. KOH.	Iodine Value. Per cent.
0·9175	thickens at −15°	186	113

BEECHNUT OIL

French—*Huile de faînes.* German—*Bucheckernoel.*
Italian—*Olio di faggio.*

For tables of constants see p. 522.

Beechnut oil is obtained from the fruit of the red beech-tree, *Fagus sylvatica*, L. The fruit consists of 33 per cent of husks and 67 per cent of kernels. The latter contain from 28 to 43 per cent of oil. The cold-drawn oil is of pale yellow colour and free from unpleasant taste. This quality of oil is used for culinary purposes, whereas the oil expressed at a higher temperature is employed as burning oil.

Beechnut oil is stated to be used as an adulterant of almond oil; its presence may be detected by determining the iodine value of the sample.

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[1] Holde, *Mitth. d. Königl. Tech. Versuchs.* 1902, 20 [2], 66. Cp. also *Ibid.* 1903, 59.

[Table

Physical and Chemical Constants of Beechnut Oil

Specific Gravity.		Solidifying Point.		Saponification Value.		Iodine Value.		Hehner Value.		Maumené Test.		Refractive Index. Oleo-refractometer.	
At 15° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	Per cent.	Observer.	° C.	Observer.	"Degrees" at 22 °C.	Observer.
0·9225	Schübler	−17	Chateau	196·3	Girard	111·2	De Negri and Fabris	95·16	Girard	65	Maumené	+16·5 to +18	Jean
0·9205	Massie			191·1	De Negri and Fabris					63	De Negri and Fabris		
0·9220	De Negri and Fabris					120·1	Wijs						

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.
17	Girard	24	Girard	114	De Negri and Fabris
		23	De Negri and Fabris		

KAPOK OIL

French—*Huile de Capock.* German—*Kapokoel.*
Italian—*Olio di Kapok.*

For tables of constants see p. 524.

Kapok oil is obtained by pressing the seeds of *Eriodendron anfractuosum* (or *Bombax pentandrum*), a tree indigenous to the tropics, and growing in great profusion in the East and West Indies and South America. The seeds are of the size of peas; they are enclosed in a hard black shell, constituting about 40 per cent of the seeds. The plant is related to the cotton plant, and the hairs covering the fruit resemble cotton, although they have neither the strength nor the staple of the latter.[1]

The seeds are free from hairs, and hence do not offer the difficulty cotton seed presents to the seed-crusher. A light crushing between rollers and winnowing through sieves, assisted by a current of air, separates the husk from the kernel. The seed is crushed on a commercial scale in Holland; the yield of the oil from the whole seed is 17·8 per cent on a manufacturing scale, whilst by extraction with ether 24·8 per cent of oil are obtainable.

The oil has a greenish-yellow colour and a not unpleasant taste and odour.

The numbers given in the table of constants show very great differences, especially as regards the saponification and iodine values. The great resemblance of this oil to cotton seed oil indicates that the iodine value 75·5 to 68·5 must be accepted with reserve, the iodine value of 117·9 to 119·4 being the more reliable one. On the other hand, *Henriques'* saponification value appears to be too low; the number 196·5, given by *Philippe*, agrees with the percentage of insoluble fatty acids, yet the *Reichert* value stated by *Philippe* cannot be reconciled with both the saponification and *Hehner* values he has ascertained. Again, the high saponification value stated by *Durand* and *Baud* agrees better with the *Reichert* value. The discrepancy in the saponification value, as given by the different observers, may find its explanation in the occurrence of hydroxylated acids, which readily form lactones, as is clearly indicated by the high acetyl value, in conjunction with the remarkably low neutralisation value of the mixed fatty acids found by *Philippe*. The neutralisation value given by *Henriques* seems, however, to exclude the presence of lactonic acids. Renewed examination of the oil is therefore desirable.

The mixed fatty acids consist, according to *Philippe*, of 30 per cent solid fatty acids, and 70 per cent liquid fatty acids as determined by the lead-salt-ether method. The solid acids consist exclusively of palmitic acid. On standing, kapok oil deposits "stearine"

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[1] *Journ. Soc. Arts*, 1893, 1030; *Journ. Soc. Chem. Ind.* 1894, 147.

Physical and Chemical Constants of Kapok Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Reichert Value.		Hehner Value.		Maumené Test.		Refractive Index. Oleo-refractometer at 40° C.	
At ° C.		Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	C.	Observer.	"Degrees"	Observer.
15 18 100	0·9237 0·9199 0·8613	Philippe[1] Henriques[5] Durand and Baud[2]	29·6	Durand and Baud	181 196·5 205·0	Henriques Philippe Durand and Baud	117·9-119·4 75·5 (?) 68·5 (?) 129	Henriques Philippe[1] Durand and Baud (?[4])	3·3	Philippe	94·9 95·4	Henriques Philippe	95	Henriques[3]	51·3	Durand and Baud

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.			Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Acetyl Value.		Iodine Value.	
At ° C.		Observer.	° C.	Observer.	° C.	Observer.	Mgrms. KOH	Observer.		Observer.		Observer.	Per cent.	Observer.
18	0·9162	Henriques	23-24 31·5 32	Henriques Philippe Durand and Baud	29 35·5-36	Henriques Philippe	191 134·6 190	Henriques Philippe (?[4])	293	Henriques	86	Philippe	108 122·5	Henriques (?[4])

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[1] *Moniteur Scientifique*, 1902, 728 (the oil was obtained by cold pressing).
[2] *Ann. Chim. anal. appl.* 8, 1903, 328 (the oil was extracted with ether).
[3] By Archbutt's process.
[4] *Chem. Revue*, 1902, 274.
[5] *Journ. Soc. Chem. Ind.* 1894, 258.

like cotton seed oil. The great resemblance of kapok oil to cotton seed oil is further accentuated by the great similarity of the colour reactions of the two oils. Thus kapok oil gives with nitric acid a similar reaction to that which cotton seed oil shows; in the case of kapok oil the tint is stated to be more greenish-brown than reddish brown. It is, however, noteworthy that the most characteristic colour reaction of cotton seed oil—the *Halphen* test—is also given by kapok oil. This fact deserves attention on the part of the analyst.

Kapok oil is used in its home for edible purposes. Seeds imported from Java are crushed in Holland, and the oil is used in soap making as a substitute for cotton seed oil.

COTTON SEED OIL

French—*Huile de Coton.* German—*Baumwollsamenoel, Cottonoel.*
Italian—*Olio di Cotone.*

For tables of constants see pp. 526-528.

Cotton seed oil is obtained on a very large scale from the seeds of the various kinds of the cotton trees, *Gossypium.* The species cultivated extensively in the United States and in Egypt is *Gossypium herbaceum.* During the latter years East India (Bombay) seed, as also Levantine (Smyrna, Mersyne, Alexandretta) seed has come into the market.

An examination made in my laboratory yielded the following results:—

Oil contained in Cotton Seeds (*Lewkowitsch*)

Kind of Seed.	Kernels. Per cent.	Husks. Per cent.	Oil from		
			Whole Seed. Per cent.	Kernels. Per cent.	Husks. Per cent.
Egyptian (1899)	60·0	40·0	21·98	37·41	
,, (1900)	60·06	40·2	23·93	38·7	0·67
Mersyne	44·4	54·8	18·67	37·44	1·2
Bombay	51·0	49·0	20·56	39·28	1·08
American			23·46		

It will be seen that the Levantine (Mersyne) seed yields the lowest percentage of oil. In this connection, it is noteworthy that the American and Egyptian seed grown at Bokhara contains 17·5 per cent of oil only.

Cotton seed is covered with woolly hairs, yielding the well-known cotton fibre. In the case of Egyptian cotton seed this fibre is easily removable by means of suitable delinting machines, so that the seed can be crushed and pressed without previously removing the

Physical and Chemical Constants of Cotton Seed Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Hehner Value.	
At ° C.		Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	Per cent.	Observer.
15	0·922-0·930	Allen	3 – 4	Lewkowitsch	191-196·5	Allen	106	Hübl	95·87	Bensemann
..	0·9228	Valenta	Below 12° "stearine" separates out from the oil.		196	Dieterich	108·7	Moore	96·17	Lengfeld and Paparelli
..	0·9222	Thomson and Ballantyne			191·6-193·5	Thomson and Ballantyne	106·8-108·3	Thomson and Ballantyne	95·9	Lewkowitsch
,,	0·923-0·925	De Negri and Fabris			191·8-193·8	De Negri and Fabris	100·9-116·9[1]	Wiley		
,,	0·923-0·926	Shukoff			192-194·5[4]	Shukoff	106·9-110	De Negri and Fabris		
18	0·9203	Long					106·5-108[2]	Wallenstein and Finck		
,,	0·9230	Stilurell					106·8[3]			
99 (water at 15·5 = 1)	0·8725	Allen					105-110	Lewkowitsch		
							106-111	Wijs		
							112-116[4]	Shukoff		
100	0·8672	Leone and Longi								

[1] American oil. [2] Egyptian oil. [3] Peruvian oil. [4] Samarkand oil.

Physical and Chemical Constants of Cotton Seed Oil—continued

Thermal Tests.			
Maumené Test.		Heat of Bromination.	
° C.	Observer.	° C.	Observer.
75-76 74-75 68-70 80-90 50-53	Archbutt Allen Del Torre Wiley De Negri and Fabris	19·4	Hehner and Mitchell
Specific Temperature Reaction.			
169-170	Thomson and Ballantyne		

Refractive Index.		
At ° C.		Observer.
15 15·5 60	1·4743-1·4752 1·4737-1·4757 1·4570	Strohmer Tolman and Munson Thoerner
Oleo-refractometer.		
"Degrees" at 22° C.		Observer.
+20 +17 to +23		Jean Pearmain
Butyro-refractometer.		
° C.	"Degrees."	Observer.
15·5 25 ,, 40	72·3-75·6 67·8 67·6-69·4 58·4	Tolman and Munson Beckurts and Seiler Mansfeld White

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.			Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molec. Weight.		Iodine Value.		Refractive Index.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.	At 60°C.	Observer.
15·5 (water at 4=1)	0·92055-0·9219	Crampton	32	Allen	35·2	Allen	203·9	Valenta	275	Valenta	110·9-111·4	Morawski and Demski	1·4460	Thoerner
40 (water at 4=1)	0·90497-0·90612	,,	30·5	Hübl	35	Hübl	208	Dieterich			115·7	Williams		
50 (water at 4=1)	0·89861-0·89972	,,	35	Bach	38	Bach	201·6	Thoerner			112·8-113	De Negri and Fabris		
100 (water at 4=1)	0·86542-0·86774	,,	36	Dieterich	38·5	Dieterich					112-115	Thoerner		
99 (water at 15·5=1)	0·8467	Allen	39-40	Bensemann [1]	42-43	Bensemann [1]					Iodine Value of the Liquid Fatty Acids.		Refractive Index of the Liquid Fatty Acids.	
100 (water at 100=1)	0·8816	Archbutt	32-35	Thoerner	35-40	Thoerner								
			Titer Test.								147·3-147·5[4]	Wallenstein and Finck	Butyro-refractometer.	
											146·8-148·2[5]			
			32·2-32·7[2]	Lewkowitsch	34-35	De Negri and Fabris					147·8[6]	,,		
											149[5]	Lewkowitsch		
			33·3-34·1[2]	,,	35-37	,,					141·9-144·5	Bömer		
			33·0-33·3[2]	,,	37-38	,,					148·9-151·7[7]	Tortelli and Ruggeri	At 48°C.	
			34·4-35·2[2]	,,							147·3[8]			
			33·3-35·0[2]	,,										
			35·6-37·6[3]	,,									53·7-51·4	Bömer
			28·1-28·5[9]	,,										

[1] Determined by Bensemann's method, cp. p. 175. [2] Part of the "stearine" taken out of the oil. [3] All the "stearine" left in the oil. [4] American oil. [5] Egyptian oil. [6] Peruvian oil. [7] Iodine value of oil 107·9-110·1. [8] Iodine value of oil 105·3. [9] Winter oil.

husk. In the case of American seed, and especially of Bombay seed, the cotton fibre so tenaciously adheres to the husk that the usual delinting machines are unable to remove the whole of the hairs; notably in the case of Bombay seed, a fine "down" adheres to the husk. Such seeds are decorticated in decorticating machines before crushing, and the kernels are separated from the husks by means of another set of machines. Chemical processes for removing the "down" are resorted to less frequently. The principle underlying these chemical processes is the same that is employed in carbonising "union" (wool and cotton) rags.

The kernels are permeated with cells containing deep brown colouring matter; hence the crude cotton seed oil as running from the hydraulic presses has a ruby-red to almost black colour. On saponifying the crude oil with caustic potash, the upper layers which are exposed to the air become blue and afterwards violet—a very characteristic reaction of crude cotton seed oil. If alkali be used in insufficient quantity to produce complete saponification, the colouring matter is carried down together with the soap formed, so that the supernatant oil is but slightly yellowish.

On this reaction is based the technical method of refining cotton seed oil. The oil is warmed (to 120° F.) and then intimately intermixed with dilute caustic soda solution, the proportion of caustic soda required depends on the quality of the oil; only so much caustic soda should be added as to combine with the colouring matter and the free fatty acids in the oil. Sufficient caustic soda has been added if a sample examined on a glass plate appears "broken." Caustic soda when applied in excess causes saponification, and in that case the whole mass is apt to form a homogeneous mixture, which very frequently refuses to separate into two layers. If a judicious amount of caustic soda has been added, the mixture will readily separate on standing into two layers. The upper layer consists of decolourised oil; the lower one forms a black to light brown heavy liquid—"mucilage,"—this being a solution of dark brown colouring matter in the soap resulting from the union of free fatty acids and caustic soda. The supernatant oil is then drawn off and washed with warm water. If the oil be intended for edible purposes it must not be bleached with chemicals, whereas for commercial purposes —"soap oil"—the oil is bleached with bleaching powder and mineral acid, and then washed with water until the mineral acid has been removed completely.

Since alkalis are used in refining cotton seed oil, the fact that commercial cotton seed oil is practically free from fatty acids is readily explained.

Cotton seed oil is a suitable oil for edible purposes, but popular prejudice has hitherto largely militated against the edible quality being sold under its true name. Hence, the oil has appeared in the market under the disguise of such names as "table oil," "salad oil," "sweet nut oil," "butter oil," etc. Enormous quantities of the "butter oil" quality are used in the manufacture of margarine and compound lards. The commercial brands "summer oil" and "winter oil" differ in that the winter oil has the bulk of the "stearine" removed, so that the oil should remain fluid, even during the winter. Such winter oil or "demargarinated" oil is characterised by a low titer test. Thus the titer test of a sample of demargarinated oil manufactured by the writer on a commercial scale was 28·1°-28·5° C.

As a by-product of winter oil there is obtained "cotton seed stearine"[1] (French—*Margarine de coton, Margarine végétale.* German—*Baumwollstearin, Vegetabilisches Margarin.* Italian—*Margarina di cotone*), a light-yellow fat of buttery consistency. This cotton seed stearine is manufactured on a large scale, especially in the United States, by cooling cotton seed oil, draining off or filtering off the solid deposit, and pressing the latter.

Since cotton seed stearine forms an article of commerce, and is largely used in the manufacture of lard and butter substitutes, it may be of use to record the physical and chemical characteristics (see tables, pp. 531, 532).

It should be noted that, according to the pressure employed in the manufacture, cotton seed stearine will contain a larger or smaller proportion of liquid glycerides; hence, the great divergence of the solidifying and melting points recorded in the table is easily explained. The behaviour of cotton seed stearine in the colour tests is the same as that of cotton seed oil itself. The same holds good of the chemical composition, with this limitation, however, that the proportion of solid fatty acids is somewhat larger than in cotton seed oil. Thus *Hehner* and *Mitchell* found in a sample of cotton seed oil 3·3 per cent of stearic acid.

According to the amount of "stearine" left in the oil, the proportion of glycerides of solid fatty acids in cotton seed oil will vary; therefore such widely different percentages of solid fatty acids as stated by *Twitchell*, *Farnsteiner*, *Tolman* and *Munson*, viz. from 22·3 to 32·6 per cent, are readily explained. The solid fatty acids consist chiefly of palmitic acid; small quantities of stearic acid have also been identified. No linolenic hexabromides having been obtained from cotton seed oil, linolenic acids may be considered as absent. The liquid fatty acids seem to consist of oleic and linolic acids only. The proportion of linolie acid in the mixed fatty acids calculated from the isolated linolic tetrabromide was found 18·45 per cent (*Farnsteiner*), and 21 per cent (*Lewkowitsch*). From the liquid fatty acids *Farnsteiner* obtained linolic tetrabromide corresponding to 23·9 per cent linolic acid. From the percentage composition of 23·45 per cent linolic acid and 76·55 per cent oleic acid would follow the calculated iodine value of the liquid fatty acids =111·5. Since direct experiments (cp. table, p. 528) lead to the approximate iodine value of the liquid fatty acids of about 150, the amount of linolic tetra-

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[1] With the above described cotton seed stearine there must not be confounded the cotton seed "stearine" obtained by distilling the fatty acids obtained from cotton seed oil "mucilage" (cp. chap. xvi.)

Physical and Chemical Characteristics of Cotton Seed Stearine

Specific Gravity.			Solidifying Point.		Melting Point.		Saponific. Value.		Iodine Value.		Hehner Value.		Maumené Test.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	Per cent.	Observer.	°C.	Observer.
15	0·91884	Crampton	31-32·5	Allen	40	Allen	194·6	Hart	89·8	Allen	95·5	Muter	48	Hart
37·7	0·9115-0·912	Muter	...	...	32·2	Muter	194·8-195·1	Lewkowitsch	93·6	Hart	96·3	Hart		
40	0·90313	Crampton												
50	0·89671	,,												
99 (water 15·5=1)	0·8684	Allen	...	...	39	Mayer	...	...	88·7	De Negri and Fabris	...	...		
100	0·867	Hart	...	...	30-31	Hart								
,,	0·86463	Crampton	16-22	De Negri and Fabris	26-29	De Negri and Fabris	...	...	92·7-92·8 99·2-103·8	Lewkowitsch Schweitzer and Lungwitz	...	...		
			Titer Test.											
			16-16·05	Lewkowitsch										

bromide found would appear to be much below the truth, and further experiments are required to explain the apparent discrepancy.

Physical and Chemical Characteristics of the Mixed Fatty Acids

Solidifying Point. Titer Test.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.
34·9-35·1	Lewkowitsch	27-30	De Negri and Fabris	94·3	De Negri and Fabris

The acetyl values of various samples of cotton seed oil were found by the writer[1] to vary from 7·6 to 18, according to the state of freshness of the oil. There was, however, no strict parallelism noticeable between the amount of total volatile acids and the acetyl value.

Cotton seed oil must be considered as typifying a semi-drying oil. In the *Livache* test it absorbs 5·9 per cent of oxygen in twenty-four hours. By blowing air through cotton seed oil at a temperature of about 90°-100° oxygen is absorbed, with the formation to a small extent only of oxidised acids, the acetyl value rising at the same time considerably. This is shown in the following table.[2] (Cp. also "Blown Oils," chap. xv.).

	Specific Gravity at 15·5° C.	Total Volatile Acids per Gram in terms of Milligrams. KOH.	Oxidised Acids. Per cent.	True Acetyl Value.
Cotton seed oil . . .	0·9250	0·1	...	7·6
Cotton seed oil, blown two hours at 120° C. . . .	0·9262	2·88	0·51	11·32
Cotton seed oil, blown four hours at 120° C. . . .	0·9291	2·44	0·87	20·46
Cotton seed oil, blown six hours at 120° C.	0·9350	4·60	0·94	25·4
Cotton seed oil, blown ten hours at 120° C.	0·9346	4·16	1·28	30·84

The mixed fatty acids do not absorb oxygen as rapidly as does the oil itself. Thus in the *Livache* test, only 0·8 per cent were absorbed, as against 5·9 per cent, in the case of the oil from which the fatty acids had been derived.

In the elaïdin test a mass is obtained of pasty and buttery consistence.

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[1] Lewkowitsch, *Analyst*, 1899, 319.

[2] *Ibid.* 322.

Cotton seed oil is readily recognised by the high melting and solidifying points of its fatty acids. This characteristic difference from similar oils renders the identification of cotton seed oil a comparatively easy task. It also greatly facilitates the detection of it in other oils and fats. Thus pure maize oil can be easily distinguished from cotton seed oil by the titer test of its fatty acids. The iodine value of cotton seed oil is also important for purposes of identification. especially so the iodine value of its liquid fatty acids, although the iodine numbers are less characteristic than the solidifying and melting points.

Cotton seed oil, being one of the cheapest fatty oils, is hardly liable to adulteration. Still, at times when linseed oil and maize oil are much cheaper than cotton seed oil, admixture with these two oils may occur. Linseed oil will be detected by the higher iodine value of the sample, and notably by the hexabromide test. The detection of maize oil is a more difficult problem (cp. p. 514).

The unsaponifiable matter in cotton seed oil varies from 0·73 to 1·64 per cent, and consists to a large extent of phytosterol, in admixture with non-crystallisable colouring matters. Hence, the characteristic phytosterol crystals can but rarely be isolated in a rapid manner from the unsaponifiable matter. According to *Bömer* and, *Winter*[1] the crude phytosterol requires to be recrystallised seven or eight times, before the pure substance, melting from 136°-137° C. can be obtained. In the phytosteryl acetate test the unsaponifiable matter yields crystals melting from 123·5°-124° C.

Edible cotton seed oil is employed in immense quantities as an edible oil for the table and in the manufacture of margarine, and besides its legitimate use, for the adulteration of olive oil, lard, and, other edible oils and fats. The detection of cotton seed oil in these oils and fats thus becomes one of the most important objects of fat analysis. It is therefore not to be wondered at that the literature on that subject is very voluminous. A number of colour tests have been recommended for the identification of cotton seed oil and its detection in other oils. The opinions of various observers as to the value of one or other of these colour tests differ greatly. The divergence of these statements is in no small degree due to the difference of age and source of the specimens examined. With regard to the latter, it should be noted that American oils differ somewhat from Egyptian oils in their behaviour to the reagents used for the colour reaction.

I have examined the various colour reactions proposed, and found most of the older tests useless. Hence, they are omitted here. The few colour tests that will be discussed are certainly of assistance to the analyst, but it should be distinctly understood that colour reactions taken by themselves should not be relied upon as giving a decisive answer. At best they can only be used as a preliminary test, or as a confirmatory test.

The best colour test for the identification of cotton seed oil, and for the detection of it in other oils and fats, provided the cotton seed oil

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[1] *Zeit. für Unters. d. Nahrgs. u. Genussm.* 1901, 872.

has not been heated, is the **Halphen colour reaction.** This test is carried out in the following manner :—1 to 3 c.c. of the oil is dissolved in an equal volume of amyl alcohol; to this is added 1 to 3 c.c. of carbon bisulphide holding in solution 1 per cent of sulphur (flowers). The test-tube containing the mixture is then immersed in boiling water, and kept therein for some time. The carbon bisulphide evaporates off, and cotton seed oil gives in the course of five to fifteen minutes a deep red colouration. This colour reaction is most characteristic, and it is possible to detect thereby 5 per cent, and even less, of cotton seed oil in admixture with other oils and fats, *e.g.* olive oil or lard. In cases where the proportion of cotton seed oil is small, the test-tube must be kept in the water-bath for twenty to thirty minutes. Mixtures of olive and arachis oils containing 1 per cent of cotton seed oil gave in the writer's laboratory distinct colourations after twenty-five to thirty minutes.

The ease with which this test can be carried out, and its apparent reliability, have led to an overestimation of this very useful and important test; so much so that grave errors may be committed by those who assign to this test an exclusive importance.

It is as yet unknown what substance produces the colour reaction in the *Halphen* test, and all conjectures as to its aldehydic nature or otherwise,[1] rest on unfounded assumptions. The chromogenetic substance appears to be present in very small quantities only, and is also retained by cotton seed cake; it has the property of passing into the body fat of pigs and cattle fed with cotton cake. Hence the *Halphen* colour reaction can be obtained with lards, etc., which are absolutely free from admixed cotton seed oil.

It should further be noted that the absence of the colour reaction in the *Halphen* test does not prove the absence of cotton seed oil. For the chromogenetic substance is destroyed by heating cotton seed oil to 250° C., or even by keeping it at 200° C., for some prolonged time.[2] Cotton seed oil so treated no longer gives the *Halphen* colour reaction. Hence a negative *Halphen* test in a suspected sample is no conclusive proof of the absence of cotton seed oil. Cotton seed oil fatty acids do not show the colour test as distinctly as the oil itself. Frequently the mixed fatty acids obtained by saponifying cotton seed oil give a very faint red colouration only, or even none at all, most of the colouring matter has either been destroyed or washed away in the process of isolating the mixed acids.

Finally *Halphen's* test can no longer be considered as exclusively due to cotton seed oil. Kapok oil (p. 525) is stated to give the same colour reaction as cotton oil.

In case a negative *Halphen* test be obtained on examining a sample, and the presence of heated cotton seed oil be suspected, confirmation may in some cases be obtained by the **nitric acid** test. This

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[1] Cp. Soltsien, *Zeit. f. öffentl. Chemie*, 1899, 306; Charabot and Marsh, *Bull. Soc. Chim.* 1899, 552; Raikow, *Chem. Zeit.* 1899, 760, 892; 1900, 562, 583; 1902, 10; Gill and Denison, *Journ. Amer. Chem. Soc.* 1902, 397. See also footnote, p. 537.

[2] Oilar (*Amer. Chem. Journ.* 24, 355) states that heating for one hour to 140°-150° C. in a steel pan suffices to nullify the Halphen colour test.

test is best carried out with nitric acid of 1·375 specific gravity, as I have ascertained by a number of experiments. A few c.c. of the sample are shaken energetically with an equal measure of nitric acid of the specified gravity, and the sample allowed to stand for some time, up to twenty-four hours. Cotton seed oil gives a coffee-brown colouration which is characteristic of this oil to such an extent that admixtures of 10 to 20 per cent of cotton seed oil to olive oil can be detected in certain cases. But even here great circumspection is necessary, as the coffee-brown colouration given by some specimens of cotton seed oil is not characteristic of all cotton seed oils. Thus the writer has met with many American cotton seed oils that give the nitric acid test so faintly that olive oils mixed with 10 per cent of this cotton seed oil showed no coffee-brown colouration. Of importance is the observation I have made, viz. that a specimen of heated cotton seed oil which no longer gives the *Halphen* test still gives the brown colouration with nitric acid, and that also the fatty acids from this specimen of heated cotton seed oil showed distinctly the colouration. This proves incidentally that there are at least two chromogenetic substances present in cotton seed oil.

The Silver Nitrate Test.—This test was first proposed by *Bechi*, and although it has been persistently condemned by a number of observers, it is still being employed by many chemists; hence a discussion of this test must find a place here. Several years ago the Italian government appointed a special committee to inquire into the value of this test, and according to the report given by *Del Torre*, the following two reagents are required.

REAGENT I.

Silver nitrate	1·00 grm.
Alcohol, 98 per cent (by volume)	200·0 c.c.
Ether	40·0 c.c.
Nitric acid	0·1 grm.

REAGENT II.

Amyl alcohol	100 c.c.
Colza oil	15 c.c.

The test is carried out as follows:—10 c.c. of the oil under examination are mixed in a test tube with 1 c.c. of reagent I., and then shaken with 10 c.c. of reagent II. The mixture is next divided into two equal portions, one of which is put aside for comparison later on, whereas the other is immersed in boiling water for a quarter of an hour. The heated sample is then removed from the water-bath and its colour compared with that of the first portion. Presence of cotton seed oil is indicated by the reddish-brown colouration of the heated portion. *De Negri* and *Fabris* lay stress on the necessity of using the purest alcohol. The colza oil used should be "cold-drawn" oil, and only slightly coloured; it should be filtered in a hot water oven before preparing the reagent. To guard against possible errors arising from the impurity of the reagents a blank test should be instituted side by side with the actual test.

Peruzzi, *Ridolfi*, *Roster*, and *Wiley* have tested *Bechi's* method in the case of over 200 samples of cotton seed oil, and have found it thoroughly reliable, no other oil giving the brown colouration. *Holde*,[1] on the contrary, considers the test as absolutely valueless; but the experiments of *De Negri* and *Fabris*, and also tests made repeatedly by the writer (see below), prove that *Holde's* statements are too sweeping, having most likely been deduced from the observations on the particular sample he examined.

The *Bechi* test is too capricious to be recommended. Moreover it is difficult to understand why colza oil is introduced; frequently even serious errors are thereby caused.

The statements contained in the literature on *Bechi's* test are of a most conflicting nature.

Benedikt found that some samples of cotton seed oil do not reduce *Bechi's* reagent either with or without the addition of colza oil. Since *Bechi* himself states that old samples of cotton seed oil only reduce the silver nitrate when colza oil has been added, the value of all the modifications proposed becomes doubtful.[2] The writer has examined mixtures of Egyptian cotton seed oil with olive oil, and finds that an admixture of 10 per cent of cotton seed oil can be detected with certainty, whereas in the case of 5 per cent the reaction becomes indistinct. The silver nitrate test can, therefore, only be relied upon as decidedly indicating presence of cotton seed oil if a positive reaction has been obtained. Absence of colouration, however, does not prove absence of cotton seed oil. Since, according to *Wesson*, pure lard (*q. v.*) gives a slight colouration with silver nitrate, and furthermore, as olive oils are often met with which give the *Bechi* reaction to a very marked extent (*Tortelli* and *Ruggeri*), even the appearance of a brown colour should not be considered as absolute proof of adulteration with cotton seed oil.

Milliau modifies *Bechi's* test by adding the silver solution to the **mixed fatty acids** instead of to the neutral oil.

Milliau[3] proceeds as follows:—5 c.c. of the fatty acids of the sample are dissolved in 15 c.c. of 95 per cent alcohol, and heated in a water-bath to 90° C., when 2 c.c. of a 30 per cent solution of silver nitrate are added, and the mixture is again heated until about one-third of the alcohol has evaporated. If the sample be cotton seed oil, or contain cotton seed oil, the silver nitrate is reduced to a metallic state, producing a black or brown colour in the liquid, or giving particles of reduced silver. Even 1 per cent of cotton seed oil, as *Milliau* states, can thus be detected. *Wiley*[4] considers this

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[1] *Journ. Soc. Chem. Ind.* 1892, 637.

[2] Wilson also (*Chem. News*, 59, 99) states that cotton seed oil, after keeping for some time, loses its power of reducing silver nitrate.

[3] *Compt. rend.* 106, 550; *Journ. Soc. Chem. Ind.* 1893, 716.

[4] *Lard and Lard Adulterations.* Washington, 1889, 467.

test a very useful one, whereas *Hehner*[1] sees no advantage in this modification of *Bechi's* test, an opinion in which I fully concur. In many samples, where cotton seed oil was present and was indicated by *Bechi's* test, no reaction was obtained.

This fact is explained by an observation made by a French committee, consisting of *Muntz*, *Durand*, and *Milliau*, viz. that by washing the free fatty acids repeatedly, the products (supposed to be of an aldehydic nature) which produce the colour reactions are washed away. In order to retain the chromogenetic substance in the mixed fatty acids, *Jean* proposes to decompose the soap solution obtained on saponifying the oil under petroleum ether. The fatty acids, as they are liberated, pass into the petroleum ether, carrying with them the chromogenetic substance; when the petroleum ether solution is subsequently washed, the chromogenetic substance is not removed.

The reduction of silver nitrate is stated to be effected by a substance of an aldehydic nature, the properties of which have not yet been investigated.[2] It should be noted that the silver reducing substance is destroyed or oxidised by heating cotton seed oil or its fatty acids to 240° C. (*Wesson*), or even by keeping the sample or the free acids for some time. Therefore, cotton seed oil heated to 240° C. cannot be identified or recognised in other fats by *Bechi's* or *Milliau's* tests.

Tortelli and *Ruggeri*[3] state that the *Milliau* test becomes more delicate on testing the liquid fatty acids in the following manner:—5 grms. of the liquid fatty acids of the suspected sample are dissolved in 10 c.c. of alcohol, and 1 c.c. of a 5 per cent silver nitrate solution is added; the sample is then heated on a water-bath to 70°-80° C. Cotton seed oil reduces the silver immediately, whereas olive oil and other oils remain clear for some time. Even cotton seed oils —which had been heated to 250° C. for ten and twenty minutes respectively — could be recognised when present in as low a proportion as 10 per cent in olive oil on allowing the liquid fatty acids of the mixed oil to stand in the hot water-bath for several hours.

From the foregoing remarks it is obvious that the colour tests can only be used as subsidiary, or at best as confirmatory tests, and that the *Halphen* test should be supplemented in the case of heated oils by the nitric acid test or by the modified *Milliau's* test described by *Tortelli* and *Ruggeri*. The main attention of the analyst should be paid to the indications furnished by the iodine value of the oil (or its mixed fatty acids), the iodine value of the liquid fatty acids, the solidifying and melting points of the mixed fatty acids, and in case an animal oil or fat is suspected of being adulterated

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[1] *Analyst*, 13, 165.

[2] Dupont (*Journ. Soc. Chem. Ind.* 1895, 811) ascribes the Bechi reaction to the formation of silver sulphide, he having obtained on passing a current of steam through cotton seed oil a volatile substance yielding sulphuric acid on oxidation. But as the remaining oil still gave the Bechi test, proof for *Dupont's* opinion is wanting.

[3] *Annali del Laborat. Centr. delle Gabelle*, 1900.

with cotton seed oil, the examination of the unsaponifiable matter by the phytosteryl acetate test. Further information on the detection of cotton seed oil will be given under the headings of "Olive Oil," "Lard," "Tallow"; cp. also "Edible Oils and Fats" in Chapter XV.

It has been pointed out already that the finer grades of cotton seed oil are used for edible purposes. The lower grades of oil are employed in enormous quantities as a soap-making oil. On account of its drying and gumming properties cotton seed oil cannot be recommended as a lubricating oil. It is stated that the blown cotton seed oil (see chap. xv.) is suitable for lubricating purposes.

SESAMÉ OIL (GINGILLI OIL, TEEL OIL)

French—*Huile de sésame.* German—*Sesamoel.*
Italian—*Olio di sesamo.*

For tables of constants see pp. 539, 540.

Sesamé oil is obtained from the seeds of the sesamé plant, *Sesamum orientale* and *Sesamum indicum*, belonging to the family of *Bignoniaceæ.*

The plants are largely grown in India, China, Japan, in the Levant, and in West Africa. Very little seed reaches this country, it is pressed chiefly in the South of France. The yield of oil is from 50-57 per cent.

The cold pressed oil has a light yellow colour, is free from odour, and has a pleasant taste, so much so that the best brands are considered equal to olive oil as an edible oil. The oils of second and third expression are used for manufacturing purposes, chiefly in soap-making.

Sesamé oil contains, according to *Farnsteiner*, 12·1 per cent to 14·1 per cent of solid acids; *Lane*[1] obtained by the lead-salt-ether method 78·1 per cent liquid fatty acids. These consist of oleic and linolic acids. Direct determination of linolic acid (by means of the linolic tetrabromide) gave 16·4, 15·2, and 12·6 per cent linolic acid. From the composition of 12·1 per cent solid acids, 15·8 per cent linolic acid, and 72·1 per cent of oleic acid, there would be calculated as the iodine value of the mixed fatty acids 93·6, whereas direct determination gave the mean value of 111. According to the above-given composition the liquid fatty acids would consist of 82 per cent of oleic acid, and 18 per cent linolic acid. This would lead to 106·4 as the calculated iodine value of the liquid fatty acids, whereas direct determinations have given the mean figure of 133. Also this calculation (cp. Cotton Seed Oil) shows that the linolic tetrabromide cannot have been fully recovered.

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[1] *Journ. Soc. Chem. Ind.* 1901, 1083.

Physical and Chemical Constants of Sesamé Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Reichert Value.		Hehner Value.		Thermal Tests.		Refractive Index.		
At °C.		Observer.	°C.	Ob-server.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Ob-server.	Maumené Test.		At °C.		Observer.
15	0·9230-0·9237	De Negri and Fabris	−5	Girard	194·6	Longi and Leone	106	Hübl	0·35	Medicus and Scherer	95·86	Bensemann	°C.	Observer.	15	1·4748-1·4762	Strohmer
15	0·924-0·926	Shukoff[1]	−4 to −6	De Negri and Fabris	187·6-191·6	Filsinger	108-111·7	Dieterich			95·6	Dietzell and Kressner			60	1·4561	Thoerner
18	0·9208-0·9212	Long			188·5-190·4	De Negri and Fabris	106·4-109	Filsinger	Reichert-Meissl Value.				65	Archbutt	Oleo-refractometer.		
20	0·9170-0·9210	Wijs[2]			192-193	Thoerner	107-112	Peters									
23	0·919	Dieterich			188-190	Shukoff[1]	106·9-107·8	De Negri and Fabris	1·2	Thoerner			63-64	De Negri and Fabris	"Degrees"	Observer.	
35	0·9078-0·9098	Long					105-107	Oliveri					Heat of Bromination.		+17 to +18	Jean	
							103-105	Thoerner							+13 to +17 at 22° C.	Pearmain	
							114-115	Shukoff[1]									
							106·1-114·5	Wijs[3]					°C.	Observer.	Butyro-refractometer.		
							105·2-110·3	Wijs[4]									
							103·9-109·8	Wijs[5]					23-23·9	Bromwell and Meyer	At °C.		Observer.
															25	69	Beckurts and Seiler
															25	67-68·2	Mansfeld
															40	58·2-59·5	Utz

[1] Russian oils.

[2] One specimen (from Curaçao seed) had the specific gravity 0·9210.

[3] One specimen (from Curaçao seed) had the iodine value 116·8.

[4] Oils of second expression.

[5] Oils of third expression.

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.
22·3	Hübl	26	Hübl	199·3	Valenta	286	Valenta	108·9-111·4	Morawski and Demski
28·5	Dieterich	31·5	Dieterich	201·6	Thoerner			111·8-112	De Negri and Fabris
18·5	Allen	23	Allen					110-111	Thoerner
25-26	Bensemann[1]	29-30 21-30	Bensemann[2] Peters					Liquid Fatty Acids.	
20-22	De Negri and Fabris	24-26	De Negri and Fabris						
23·5	Thoerner	25-32	Thoerner					139·9	Lane
Titer Test.								130·9-136·3[3]	Tortelli and Ruggeri
22·9-23·55 23·7-23·8 21·2-22·93	Lewkowitsch ,, ,,							129·4[4]	,,

Refractive Index.		
At 60° C.		Observer.
1·4461		Thoerner
Butyro-refractometer.		
°C.	"Degrees."	Observer.
25	53·2-54	Utz
40	45·1-47·2	,,

[1] Point of incipient fusion.

[2] Point of complete fusion.

[3] Iodine value of oil, 108·6-113·7.

[4] Jaffa oil ; iodine value of oil, 109·5.

Sesamé oil is dextro-rotatory, a property which may be found useful as an additional means of identifying the oil. The numbers ascertained by *Bishop* have been given above (chap. v. p. 210). *Utz*[1] determined the rotations of three specimens of African, Indian, and Levantine oils in a 200 mm. tube at 15° C. and found the respective rotations + 1·6°, + 1·4°, and + 0·8°. It should, however, be noted that only in the absence of castor, croton, and rosin oils would the polarimetric observation be of any use. The optical activity of the oil is no doubt due to the presence of phytosterol and sesamin (see below).

The amount of unsaponifiable matter in sesamé oil varies from 0·95 per cent to 1·32 per cent. The unsaponifiable matter contains phytosterol, sesamin, and a so-called red oil (see below). The phytosterol was identified by the melting point of the crystals obtained by crystallising it seven times from alcohol. The phytosteryl acetate obtained from the phytosterol had the melting point 128°-129° C. According to *Tocher*[2] glacial acetic acid extracts from sesamé oil two substances—

(*a*) A resinous substance which forms long crystalline needles (from alcohol), melting at 118° C. From a number of ultimate analyses and from determinations of the molecular weight (by *Raoult's* method in benzene and acetic acid) the formula $C_{18}H_{18}O_5$ was derived. This substance was named *sesamin*. Sesamin does not give the *Baudouin* test (see below), but assumes a green and then bright red colour with nitro-sulphuric acid (the colour reaction given by the U.S. Pharmacopœia for sesamé oil).

(*b*) A thick brown oil (of unknown composition) which gives the characteristic colour reactions of sesamé oil.[3]

Villavecchia and *Fabris*[4] state that by extracting the oil itself with either acetic acid or alcohol the chromogenetic substance cannot be wholly removed. By converting the oil into barium soap, and extracting the latter with alcohol, these chemists isolated from the alcoholic extract, by evaporating off the alcohol, and dissolving the residue in petroleum ether, three substances—

1. A higher alcohol of the melting point 137° C., and rotatory power $[\alpha]_D^{20} = -34° 23'$, for $c = 5·013$. This alcohol is doubtless phytosterol.

2. A substance forming beautiful crystals of the formula $(C_{11}H_{12}O_3)_2$, melting point 123° C. (*Villavecchia* and *Fabris*); $C_{33}H_{30}O_{10}$, melting point 122·5° C. (*Bömer* and *Winter*); its rotatory power is $[\alpha]_D = +68·36$, for $c = 24·45$ in chloroformic solution. This substance was termed *sesamin* by *Villavecchia* and *Fabris*. It is apparently identical with *Tocher's* sesamin $C_{18}H_{18}O_5$, for theory requires for $C_{18}H_{18}O_5$, $C = 68·79$ per cent, $H = 5·73$, and for $C_{11}H_{12}O_3$,

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[1] *Pharm. Zeitg.* 45, 490 ; *Journ. Soc. Chem. Ind.* 1900, 914.

[2] *Pharm. Journ. and Trans.* 1891, 639 ; 1893, 700.

[3] Merkling's (*Journ. Soc. Chem. Ind.* 1888, 45) statement that it is the glacial acetic acid extract which gives the characteristic colour reaction of sesamé oil requires therefore correcting.

[4] *Journ. Soc. Chem. Ind.* 1894, 69.

C = 68·75, H = 6·25, and for $C_{33}H_{30}O_{10}$, C = 67·54 per cent, H = 5·17 per cent. *Tocher* found (by *Raoult's* method) the molecular weight of sesamin 311 (in benzene) and 312 (in acetic acid). *Villavecchia* and *Fabris*[1] obtained the molecular weight by *Raoult's* method 350 (in benzene), the formula $(C_{11}H_{12}O_3)_2$ demanding 384; *Bömer* and *Winter's* proposed formula $C_{33}H_{30}O_{10}$ leads to a molecular weight of 586.

3. A thick, non-crystallisable oil, free from nitrogen. This oil contains the substance which produces the characteristic reaction with sugar and hydrochloric acid (see below), a very minute quantity giving the crimson colour with these reagents (cp. *Tocher's* substance (*b*)). It should be noted that this chromogenetic substance entirely passes into the liquid fatty acids, if the latter be prepared by the lead-salt-ether method, in contradistinction to those olive oils (see below) which simulate sesamé oil in the *Baudouin* test (*Tortelli* and *Ruggeri*[2]).

The last-mentioned **colour reaction** is extremely characteristic of sesamé oil, so that it can thereby be detected with certainty in mixtures with other oils. This test, due to *Camoin*, generally, however, known as the *Baudouin* reaction, is the only colour reaction which has hitherto been found absolutely reliable in the analysis of oils and fats. This colour reaction is all the more valuable as the chromogenetic substance is not destroyed by heating the oil to 250° C. for twenty minutes (*Tortelli* and *Ruggeri*). *Baudouin's* test is usually carried out in the form recommended by *Villavecchia* and *Fabris.*

Baudouin's Test, as recommended by Villavecchia and Fabris.—Dissolve 0·1 grm. of sugar in 10 c.c. of hydrochloric acid of spec. grav. 1·19 in a test-tube, and 20 c.c. of the oil to be tested, shake thoroughly for one minute and allow to stand. The aqueous solution separates almost immediately. In the presence of even the smallest quantity of sesamé oil it will be found coloured crimson.

Villavecchia and *Fabris*[2] attribute the chromatic reaction to the agency of levulose, or of substances produced by the action of hydrochloric acid on the latter; therefore glucose, maltose, and galactose cannot be used in place of saccharose. The main product of the interaction of levulose and hydrochloric acid being furfural, these authors accordingly substitute the latter for the mixture of sugar and hydrochloric acid. Inasmuch as furfural itself gives a violet tint with hydrochloric acid, it is necessary to use a dilute solution; it has been found best to employ a 2 per cent alcoholic solution of furfural. The modified test is carried out in one of the following two forms:—

(*a*) Place 0·1 c.c. of the 2 per cent furfural solution in a test-tube, add 10 c.c. of the oil to be tested, and 10 c.c. of hydrochloric acid of spec. grav. 1·19, shake the mixture for half a minute and allow to settle. In the presence of sesamé oil, even if it be less than 1 per cent, the aqueous layer will acquire a distinct crimson colour.

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[1] *Annali del Lab. Chim. delle Gab.* iii. 1897, p. 22.

[2] *Journ. Soc. Chem. Ind.* 1894, 69.

In the absence of sesamé oil the lower layer is either colourless, or has at most, as in the case of a very rancid though pure olive oil, a dirty yellow colour.

(*b*) Mix, as above, 0·1 c.c. of the alcoholic furfural solution with 10 c.c. of oil, and add 1 c.c. only of hydrochloric acid, agitate thoroughly and induce separation by addition of 10 c.c. of chloroform, when the aqueous layer will float on the top. Even less than 1 per cent of sesamé oil will be indicated by the crimson colouration of the aqueous layer.

These two methods have been tried on a large number of olive and arachis oils obtained from various localities, and further on rape (colza), cotton seed, linseed, walnut, poppy seed, neat's foot, blubber, and fish oils, and their absolute reliability has been confirmed.[1] With regard to olive oils it should be noted that some Tunisian, Algerian, and Portuguese olive oils from Douro (*Domergue*, *Burker*, *Ferreira da Silva*), as also some Italian olive oils (*Lalande* and *Tambon*) from the provinces of Bari, Brindisi, and Lecce, give a colour reaction which may lead to doubt. In such cases *Tortelli* and *Ruggeri*[2] recommend to test the liquid fatty acids, as the chromogenetic substance of such abnormal olive oils does not pass into the liquid fatty acids. Thus, distinction between such olive oils and olive oils adulterated with sesamé oil is rendered feasible.

Considering the reliability of the *Baudouin* reaction, all "modifications," and other colour reactions that have been proposed, are of no importance. Therefore they are omitted in this treatise.[3]

Recently *Kreis*[4] detected in sesamé oil a new substance, which he considers to be a phenol; hence he termed it sesamol.

The drying power of sesamé oil is much weaker than that of cotton seed oil. In the *Livache* test, after seven days only 2·4 per cent of oxygen were absorbed; under the same conditions the fatty acids absorbed 2 per cent of oxygen after eight days.

In the elaïdin test sesamé oil becomes red after a short time, and acquires a dirty reddish brown colour, yielding even after twenty-four hours' standing only a semi-fluid elaïdin.

The cold-drawn sesamé oil is largely used as an edible oil, notably so in the manufacture of margarine. Since small quantities of sesamé oil are easily revealed by the *Baudouin* test, it has been made obligatory in Germany and Austria to use at least ten parts of sesamé oil in the manufacture of margarine for 100 parts of fatty matters (cp. "Margarine," chap. xv.). In Belgium 5 per cent are obligatory. Sesamé oil is largely used in perfumery (for the extraction of balsam of Peru, etc.). The best cold-drawn oil being rather high in price,

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[1] Further confirmation is given by Wauters, *Journ. Soc. Chem. Ind.* 1896, 136.

[2] *Chem. Ztg.* 1898, 601.

[3] Cp. 2nd ed. of this work, p. 391, 370. Bellier, *Ann. chim. analyt. appliq.* 1899, 217. Bömer, *Zeit. Unters. Nahrungs. u. Genussm.* 1899, 705. Breinl, *Chem. Ztg.* 1899, 647; Vandevelde, *Bull. de l'Ass. Belge*, 1900, May. Kreis, *Chem. Zeit.* 1902, 1014; 1903, 316. Tambon, *Journ. Pharm. et Chem.* 1901, 57. Utz, *Chem. Revue*, 1902, 177; *Journ. Soc. Chem. Ind.* 1902, 1196.

[4] *Chem. Zeit.* 1903, 1030.

adulteration of the best qualities with poppy seed oil, cotton seed oil, and arachis oil is not infrequent. The sesamé oils of second and third expression are adulterated with rape oil.

Poppy seed oil is detected by a higher iodine value than the normal one. For the detection of *cotton seed oil* the melting and solidifying points of the fatty acids should be resorted to. The iodine value of an *oil* adulterated with cotton seed oil has not led to a decisive importance. The iodine value of the liquid fatty acids, as also the determination of the tetrabromide, carried out under the conditions described in Chapter VIII., would afford more reliable information. As confirmatory tests, the colour reactions of cotton seed oil described above should be resorted to.

Arachis oil is detected by the isolation of arachidic acid. The addition of arachis oil would lower the specific gravity of the sample.

The presence of *rape oil* would be ascertained by the lower specific gravity of the sample, lower solidifying and melting points of the fatty acids, and notably the lower saponification value.

Sesamé oil is in its turn used as an adulterant of fatty oils, notably of poppy seed oil. Admixture of sesamé oil with other oils is, however, little practised since the detection of the smallest quantity of sesamé oil is rendered easy by the *Baudouin* test.

The lower qualities of sesamé oil find a large outlet for soapmaking in the south of Europe; they are also used as burning oil.

BASSWOOD OIL[1]

French—*Huile de tilleul.* German—*Lindenholzoel.*
Italian—*Olio di tiglio.*

Physical and Chemical Constants of Basswood Oil

Specific Gravity.	Solidifying Point.	Saponific. Value.	Iodine Value.
At 15° C. (Water 15° C. = 1).	°C.	Mgrms. KOH.	Per cent.
0·938	−10	178·1	111

This oil was obtained from Basswood (*Tilia Americana*) by extracting rasped wood with ether.

LEMON PIPS OIL[2]

German—*Citronenkernoel.*

On extracting dried and ground lemon pips with solvents, lemon pips oil is obtained as a pale yellow oil having a bland flavour recalling that of almond oil.

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[1] Weichmann, *Journ. Soc. Chem. Ind.* 1895, 665.

[2] W. Peters and G. Frerichs, *Arch. d. Pharm.* 1902 [240], 659; *Journ. Soc. Chem. Ind.* 1903, 102.

The sample examined by *Peters* and *Frerichs* had the acetyl value 13·65.

Physical and Chemical Constants of Lemon Pips Oil

Saponification Value.	Iodine Value.
Mgrms. KOH.	Per cent.
188·4	109·2

The fatty acids are stated to consist of palmitic, stearic, oleic, and linolic acids.

LUFFA SEED OIL

French—*Huile de Luffa.* German—*Schwammkürbiskernoel.*

Physical and Chemical Constants of Luffa Oil

Specific Gravity.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Hehner Value.	Refractive Index.
At 15·5° C. (water at 15·5 = 1.)	Mgrms. KOH.	Per cent.	c.c. $\frac{1}{10}$ norm. KOH.	Per cent.	Butyro-refractometer.
0·9254	187·80	108·51	1·43	94·80	62·0 at 40° C.

This oil is expressed in East India from the seeds of *Luffa egyptica ;* it is used by the natives as an edible oil.

The oil examined by *Crossley* and *Le Sueur* [1] was reddish brown in colour and had a slight odour.

According to *Crossley* and *Le Sueur's* experiments it is a semi-drying oil.

CROTON OIL

French—*Huile de croton.* German—*Crotonoel.*
Italian—*Olio di crotontiglio.*

For tables of constants see p. 547.

Croton oil is obtained from the seeds of *Croton Tiglium,* a tree belonging to the *Euphorbiaceæ*, indigenous to the Malabar coast, and cultivated in Southern Asia and China. The seeds contain 53-56 per cent of oil.

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[1] *Journ. Soc. Chem. Ind.* 1898. 991.

The oil has an amber-yellow, or orange, or brown colour according to age, has a nauseous odour, a burning taste, and is a very powerful purgative. According to *Kobert*[1] there are some kinds of croton oil in commerce that are miscible with *alcohol* in every proportion. This statement, however, only holds good of those oils that have been extracted from the seeds with alcohol. *Javillier*[2] states that oil obtained by expression or by extraction is only miscible with absolute alcohol if less than one volume be used; on mixing equal volumes of oil and absolute alcohol turbidity sets in, and with more alcohol complete separation into two layers is obtained, whereas oil extracted with alcohol is soluble in absolute alcohol in every proportion.

The writer has examined three specimens of croton oil prepared for pharmaceutical purposes by reliable firms. One volume of oil was shaken up with three and a half volumes of absolute alcohol. After separation into two layers had taken place, the amount of oil dissolved by the alcohol was determined quantitatively. The alcohol had dissolved from the three samples—24·4 per cent, 25·5 per cent, and 53·4 per cent respectively. The respective specific gravities of the oils were 0·9428, 0·9418, 0·9375. Hence croton oil can no longer be classed together with castor oil, and the comparative great solubility of the oil in absolute alcohol must be ascribed to the large proportion of glycerides of volatile fatty acids. The larger the proportion of free fatty acids the greater will be the solubility of the oil in absolute alcohol. Thus the above-mentioned specimen, of which 24·4 per cent dissolved in alcohol, contained 7·9 per cent free fatty acids.

Croton oil further differs from castor oil by its solubility in petroleum ether in all proportions.

The chemical composition of croton oil differs so widely from that of all other oils that its recognition by means of the quantitative reactions is easy. The writer found 0·55 per cent of unsaponifiable matter in various specimens of croton oil. According to *Peter*, croton oil is strongly dextro-rotatory.

Croton oil is stated to contain the following fatty acids, partly as free acids and partly as glycerides: Stearic, palmitic, myristic, lauric, valeric (isobutyl formic), butyric, acetic, formic, oleic, and tiglic. "Croton-oleic acid," which was said to constitute the purgative principle of the oil, and had been described as a non-volatile, unsaturated fatty acid, differing from oleic acid in that its barium salt was soluble in alcohol, is, according to *Dunstan* and *Bole*,[3] a resinous substance possessing a strong vesicating action.[4] On standing croton oil deposits some "stearine." Two samples examined by *Lewkowitsch*[5] had the true acetyl values 19·82 and 32·66 respectively.

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[1] *Chem. Zeit.* 1887, 416.

[2] *Journ. Pharm. Chim.* [6], 7, 524.

[3] *Journ. Soc. Chem. Ind.* 1895, 985.

[4] Its empirical formula is $C_{13}H_{18}O_4$; it is a hard, pale yellow, brittle resin, nearly insoluble in water, petroleum ether, and benzene, but easily soluble in alcohol, ether, and chloroform. On heating it softens gradually, and is quite fluid at 90° C. It has neither acid nor basic properties; it is decomposed by boiling with alkalis, yielding a mixture of acids, and loses thereby its vesicating properties. This seems to point to this substance being a lactone or an anhydride.

[5] *Analyst*, 1899, 319.

Physical and Chemical Constants of Croton Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Hehner Value.		Refractive Index.					
													Oleo-refractometer.			Butyro-refractometer.		
At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	°C.		Observer.	°C.		Observer.
15	0·9437	Dulière[3]	−7	Javillier	215	Lewkowitsch	106·6-109·1	Wijs	13·56	Lewkowitsch	88·9	Lewkowitsch	22	+35	Dulière	27	77·5	Dulière
15·5	0·9375[1]-0·9428[2]	Lewkowitsch			210·3	”	101·7-102[6]	Lewkowitsch	13·27	”	89·1	”				40	68	Lewkowitsch
100	0·8874	Dulière			215·6	Dulière	103·9-104·7	”	12·1	Dulière								
					192·9[4]	Javillier	109[4]	Javillier										
					194·5[5]	”	108[5]	”										

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Neutralisation Value.		Iodine Value.	
°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
18·6-19[7]	Lewkowitsch	201	Benedikt	111·2-111·8	Dulière

[1] 53·4 per cent soluble in alcohol. [2] 24·4 per cent soluble in alcohol. [3] *Journ. Soc. Chem. Ind.* 1899, 1133; *Ann. Pharm.* 1899, 5, 229.
[4] Expressed oil; acid value 27·3. [5] Oil extracted with ether; acid value 30·9.
[6] A sample recently examined had the high iodine value of 122·3 (saponification value 210·2). [7] Titer test.

Croton oil is a weak drying oil; it thickens somewhat on exposure to air. It yields no elaïdin, hence oleic acid is very likely absent. Owing to the slight similarity between croton oil and castor oil adulteration of croton oil with castor oil has occurred. Castor oil in croton oil would increase the specific gravity, lower the iodine value, and raise the acetyl value considerably.

CURCAS OIL, PURGING NUT OIL, PHYSIC NUT OIL

French—*Huile de Pignon d'Inde.* German—*Curcasoel.*
Italian—*Olio di curcas.*

For tables of constants see p. 549.

Curcas oil is obtained from the seeds of *Jatropha Curcas* (purging nut) by hot pressing. The plant is cultivated in all Portuguese colonies, and chiefly in the Cape Verd islands.[1] The fresh oil has a pale colour, but becomes yellow with a reddish tint on exposure to the air. Its unpleasant odour is characteristic, and may serve to distinguish curcas oil from other oils; it is further characterised by its strong purgative properties, which are much more pronounced than those of castor oil.

The acid values of commercial samples were found by *Lewkowitsch* and *Archbutt* 8·5 and 0·7 respectively. *Klein* obtained values varying from 0·57 to 4·96. The proportion of unsaponifiable matter—phytosterol—in the oil is 0·5 to 0·58 per cent (*Lewkowitsch; Klein*). The acetyl value was found 8·4 (*Lewkowitsch*) and 9·8 (*Archbutt*). 100 parts of absolute alcohol dissolve at 15·5° C. about 2·17 volumes of oil (*Archbutt*). *Klein* found that alcohol (specific gravity not stated) dissolves 2·41 parts. The oil is insoluble in cold glacial acetic acid, but dissolves in the hot.

On standing at a temperature of about 12° C. a small quantity of solid glycerides separate. According to *Klein* curcas oil yields about 10 per cent of solid fatty acids (melting at 57·5° C., and solidifying at 53·5° C.); the liquid fatty acids consist of about equal proportions of oleic and linolic acids as ascertained by the relative quantities of their oxidation products, viz. dihydroxystearic and tetrahydroxystearic acids. The existence of isocetic acid (p. 92), stated by *Bouis* to occur in curcas oil, is doubtful.

The oil is used for soap-making, as an illuminant, and as a lubricating oil; it can, however, hardly be considered suitable for the last-named purpose, as the oil dries in about 24 hours, cotton seed oil drying under the same conditions in 18-20 hours, and good rape oil in 48 hours (*Archbutt*).

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[1] Klein, *Journ. Soc. Chem. Ind.* 1898. 1156.

[TABLE

Physical and Chemical Constants of Curcas Oil

Specific Gravity.			Solidifying Point.		Melting Point.		Saponific. Value.		Iodine Value.		Reichert-Meissl Value.		Hehner Value.		Maumené Test.		Refractive Index.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.	At 25° C.	Observer.
15	0·9192	Horn	−8	Girard.	−4	Lewkowitsch	193·2	Lewkowitsch	100·9	De Negri and Fabris	0·55	Lewkowitsch	95·5	Lewkowitsch	65-66·6	Archbutt	1·4681-1·487	Klein
,,	0·920	De Negri and Fabris[1]	−8	Lewkowitsch														
,,	0·915	Arnaudon and Ubaldini[2]							98·3	Lewkowitsch								
,,	0·9199-0·921	Klein																
15·5	0·9204	Lewkowitsch[3]																

Butyro-refractometer.

At °C.		Observer.
25	65	Lewkowitsch
40	56·5	,,

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.	
Titer Test.	Observer.	°C.	Observer.	Per cent.	Observer.
28·6	Lewkowitsch	24-26	De Negri and Fabris	105·05	De Negri and Fabris

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[1] *Journ. Soc. Chem. Ind.* 1893, 453.

[2] *Ibid.* 1893, 934.

[3] *Chem. Revue*, 1898, 211.

BRAZIL NUT OIL

French—*Huile de noix de Brésil.* German—*Paranussoel.*
Italian—*Olio di noci del Brasile.*

For tables of constants see p. 551.

Brazil nut oil is obtained from the seeds of the Brazilian nut tree *Bertholletia excelsa.*

The oil is of pale yellow colour and odourless; its taste is similar to that of the nuts themselves.

On standing, even at the ordinary temperature, the oil deposits "stearine." A sample examined by *Niederstadt*[1] contained 16 per cent of free fatty acids. In South America brazil nut oil is expressed from the nuts for edible purposes. The nuts that have become mouldy in transit to Europe are expressed, and the oil thus recovered is used for soap-making or as a substitute for inferior kinds of olive oil.

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[1] *Ber. d. Deutsch. Pharm. Gesellsch.* 1902, 144.

[TABLE

Physical and Chemical Constants of Brazil Nut Oil

Specific Gravity.		Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.	
At 15° C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.
0·9180	De Negri and Fabris	0-4	De Negri and Fabris	193·4	De Negri and Fabris	106·22	De Negri and Fabris[1]	50-52	De Negri and Fabris
						90·6	Niederstadt		

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.
31·1-32·25[2]	Lewkowitsch	28-30	De Negri and Fabris	108	De Negri and Fabris

[1] The iodine value of Brazil nut oil extracted with solvents is given by *De Negri* and *Fabris* as 93·8-95·1.

[2] Titer test.

SORGHUM OIL

This oil has been obtained from the dried seeds of *Sorghum cernuum*, which is largely cultivated in Turkestan.

The oil is characterised by a peculiar odour, it represents a yellow, vaseline-like mass ; it has, however, greater consistence.

Physical and Chemical Constants of Sorghum Oil

Specific Gravity at 15° C.	Melting Point. °C.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Hehner Value.
0·9282	39-40	172·1	98·89	2·1	96·1

Physical and Chemical Constants of the Mixed Fatty Acids

Melting Point.	Iodine Value.
43-44	101·63
	Iodine Value of the Liquid Fatty Acids.
	148·08

This oil dries slowly ; the specimen examined by *Andrejew*[1] had an acetyl value of 6·85. The amount of lecithin calculated from a phosphorus was 0·23 per cent. According to *Andrejew*, the mixed fatty acids of the oil consists chiefly of erucic acid, and small quantities of oleic, ricinoleic, and linolic acids. These statements stand in need of confirmation.

COUMOU OIL, PATAVA OIL[2]

Coumou oil is obtained from the kernels of the following two species of palm trees : *Œnocarpus batana*, Mart., and *Œ. bacaba*, Mart. The kernels are boiled out with water, when a pale yellow limpid oil —termed "patava oil"—rises.

Physical and Chemical Constants of Coumou Oil

Saponification Value.	Iodine Value.	Reichert Value.	Hehner Value.
169·1	96·5	1·2	95·7

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[1] *Chem. Zeit. Repert.* 1903, 283.

[2] Bassière, *Journ. Pharm. Chim.* 1903, 323.

Lesser Known Semi-Drying Oils

Name of Oil.	German.	French.	Italian.	Source.	Native Country.	Yield Per cent.	Specific Gravity.	Saponification Value.	Iodine Value.	Hehner Value.	Refractive Index.	Neutralisation Value of Fatty Acids.	Solidifying Point of Fatty Acids. °C.	Melting Point of Fatty Acids. °C.	Iodine Value of Mixed Fatty Acids.	Refractive Index of Fatty Acids.	Acid Value.	Observer.
Apple seed	Apfelsamenoel	Huile de pommier	Olio di mela	Pirus malus	...	20	0·9016	202	135	93·0	1·47127 at 21° C.	288	...	...	83-86 (?)	1·47937	57·4	R. Meyer[5]
Pear seed	Birnensamenoel	Huile de poirier	Olio di pera	Pirus communis	...	15	0·9177	113 (?)	121	91·0	1·47176 at 21° C.	196	16	25	101-104	1·47078	39	,,
Orange seed	Orangensamenoel	Huile d'oranger	Olio d'arancia	Citrus aurantium	...	20-28	0·923	229 (!)	104	95·0	1·47137 at 21° C.	280 (!!)	35	40	74 (?)	1·45741 at 21° C.	38·3	,,
..	...	...	...	Joannesia princeps Vellos	Brazil	...	...	189·47	98·3	...	...	...	...	...	...	...	...	Niederstadt
...	...	...	...	Bignonia flava Vellos	,,	...	...	185·68	93·9	...	...	...	...	...	...	...	...	,,
Barley seed	Gerstensamenoel	Huile d'orge	Olio d'orzo	Hordeum vulgare	...	...	0·94744	280	90	86	...	280	...	...	63·5 (!)	1·4745 at 30° C.	25	R. Meyer[5]
...	.	...	...	Caesalpinia Bonducella Roxb.	Brazil	...	...	...	89·9	...	...	...	...	...	...	...	...	Niederstadt
Coriander seed	Coriandersamenoel	Huile de coriandre	Olio di coriandro	Coriandrum sativum	...	5	0·9019	63 (?)	88·3	98 (?)	1·4698 at 23° C.	255 (!!)	...	...	84·7	1·48729 at 29° C.	15·4	R. Meyer[5]
Fern[3]	Farrenkrautoel	...	...	Aspidium filix mas[3]	...	...	...	...	85·4	...	...	...	...	...	...	...	...	Katz[4]
Paprica	Paprikaoel	Huile de poivre de Guinée	Olio di paprica	Capsicum annuum	...	20	0·92906	270 (?)	84·5	92	1·47763 at 21° C.	...	27	30	66 (!)	...	52	R. Meyer[5]
Bean oil	Bohnensamenoel	Huile de fève	Olio di fava	Vicia fava	...	...	0·9570 at 16° C.	188	82	86·2 (?)	...	...	...	31	115 (!)	1·47529 at 26° C.	115	Katz
Rye seed	Roggensamenoel	Huile de seigle	Olio di segale	Secale cereale	...	...	0·9334	196	81·88	88·8	1·47665 at 28° C.	199	34	36	113	1·47107 at 26° C.	40·6	,,
× Laurel nut, Domba, Alexandrian laurel	...	...	...	Calophyllum inophyllum[1]	...	60	0·9315 at 16° C.	196·4	...	...	...	...	...	...	...	...	...	D. Hooper[2]

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[1] An oil from *Calophyllum inophyllum* has been described under the name *Poonseed Oil* (German, *Tacahamacfett*) as having the specific gravity 0·950, melting point 37·6, saponification value 285·6, and yielding 90·85 per cent insoluble fatty acids.

[2] *Pharm. Journ. Trans.* 1889 (19), 525; cp. also *Journ. Soc. Chem. Ind.* 1901, 642.

[3] The fatty oil from *Aspidium spinulosum* is stated by Farup (*Arch. d. Pharm.* 1904, 17) to consist chiefly of olein. About 4 per cent of linolic acid were shown to be present amongst the fatty acids. Phytosterol has also been shown to be present in the oil.

[4] The oil contains the glycerides of palmitic, cerotic, and oleic acids, the saturated acids forming about 4·5 per cent of the total fatty acids (*Archiv d. Pharm.* 1898, 655).

[5] *Chemiker Zeitung*, 1903, 958. I have added the (?) and (!) as the figures stand in need of confirmation.

Face page 553.

× See Apotheker Zeitung. 1905. p. 6.

The oil is stated to be a semi-drying oil. The sample examined contained 4·3 per cent of free fatty acids. The extremely low saponification value cannot be reconciled with the statement made by *Bassière*, that the sample yielded 10·4 per cent of glycerin, and that the molecular weight of the fatty acids was 289·1. Nor can the statement that the sample contained 19 per cent of oleic acid be correct. The mixed fatty acids melt at 19° C.

PINOT OIL, PARA PALM OIL, PARA BUTTER[1]

Pinot oil is obtained from the kernels of *Euterpe oleracea*, Mart., known as the pinot or ouassey palm in Brazil and French Guiana. In the latter country it grows in profusion in the salt marshes of the lowlands, where it replaces the mangroves. These localities are known under the name "pinotières."

The oil is obtained by crushing the kernels and boiling them with water, when the oil rises to the top. In its fresh state pinot oil is a clear, slightly perfumed oil having a pleasant flavour.

The oil is a semi-drying oil; on finely divided lead it absorbs 4·5 per cent of oxygen in four days. The fatty acids are stated to consist of 52 per cent of oleic acid and 48 per cent of solid acids. This statement is greatly at variance with the iodine value, given as 136. Also the saponification value, stated to be 162·4, stands in need of confirmation. The mixed fatty acids are stated to melt at 12° C. The sample examined was six months old, and contained 42 per cent of free fatty acids. In Brazil and Guiana the fat is used in the fresh state for edible purposes.

Lesser known semi-drying oils, see table on opposite page.

β. The Rape Oil Group

All the members of this group are obtained from seeds of plants belonging to the *Cruciferæ*.

Their drying powers are not of a marked character; the elaïdin obtained from them is a buttery mass.

Their most characteristic property is that they have a much lower saponification value than any other vegetable oil, owing to the presence of erucin in these oils. Arachidic acid also appears to form a normal constituent, this acid having been found in a large number of rape oils as also in a specimen of mustard oil.

The opinion held for a long time that these oils contain sulphur has been shown to be erroneous; all the "cold-drawn" rape oils are free from sulphur, and absence of that element in an oil does not, therefore, prove absence of rape oil. Presence of sulphur, however,

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[1] Bassière, *Journ. Pharm. Chim.* 1903, 323.

may point to a rape oil which has been expressed at a high temperature or extracted with carbon bisulphide.

I describe the following oils: Garden cress oil, ravison oil, hedge mustard oil, rape oil, black mustard oil, white mustard oil, radish seed oil, jamba oil.

GARDEN CRESS OIL

French—*Huile de cresson.* German—*Gartenkressensamenoel.*
Italian—*Olio di crescione.*

For tables of constants see p. 555.

Garden cress oil is obtained from the seeds of the garden cress, *Lepidium sativum*, L. The seeds contain from 23-25 per cent of oil.

The high iodine value of this oil, and especially its exceptionally high thermal reaction, place it nearer to the two oils from cruciferous plants described already, viz. cameline oil and garden rocket oil (drying oil), than to the other oils belonging to the rape oil group. Garden cress oil ranks, therefore, among the slowly drying oils.

In East India garden cress oil is used as an edible oil. Two specimens from Bengal and the Punjab, examined by *Crossley* and *Le Sueur*,[1] had the acid values 10·55 and 4·18 respectively.

On saponifying, the peculiar odour of the oil disappears, and an unpleasant fish-like smell is noticeable, more strongly in the case of the extracted oil than in the case of the pressed oil. On liberating the fatty acids, the original odour again becomes noticeable, although it is not so strong as in the original oil.

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[1] *Journ. Soc. Chem. Ind.* 1898, 991.

Physical and Chemical Constants of Garden Cress Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Hehner Value.		Maumené Test.		Refractive Index.		Viscosity.	
At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.	Butyro-refractometer.		Seconds at 70° F.	Observer.
15 (water at 15=1)	0·920	De Negri and Fabris	−16	Schaedler	178	De Negri and Fabris	108-108·8	De Negri and Fabris	0·44-0·22	Crossley and Le Sueur	95·57	Crossley and Le Sueur	92-95	De Negri and Fabris	At 40° C.	Observer.	321·6	Crossley and Le Sueur
15·5 (water at 15·5=1)	0·9210-0·9221	Crossley and Le Sueur[1]			181·5-183·1	Crossley and Le Sueur[1]	101·72-118·4	Crossley and Le Sueur[1]							60·5	Crossley and Le Sueur[1]		
20	0·9212[2]	Wijs			186·4[2]	Wijs	133·4[2]	Wijs										
,,	0·9221[3]	,,			185·6[3]	,,	139·1[3]	,,										

Physical and Chemical Constants of the Mixed Fatty Acids

Melting Point.		Iodine Value.		Neutralisation Value.		Mean Molecular Weight.	
°C.	Observer.	Per cent.	Observer.	Mgrms. KOH.	Observer.		Observer.
16-18	De Negri and Fabris	111·40	De Negri and Fabris	193·0[2]	Wijs	291[2]	Wijs
20-21[3]	Wijs	137·7[2]	Wijs	193·4[3]	,,	290[3]	,,
		144·9[3]	,,				

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[1] Two oils from Bengal and the Punjab respectively.

[2] Expressed oil.

[3] Extracted oil.

RAVISON OIL

French—*Huile de ravison.* German—*Ravisonoel.*
Italian—*Olio di ravizzone.*

For tables of constants see p. 556.

The oil from Black Sea rape seed, a kind of wild *Brassica campestris* (cp. Rape Oil, p. 558), is termed in commerce Black Sea rape oil or ravison oil. The seed contains 33-40 per cent of oil.

The samples of ravison oil examined by *Archbutt* and *Deeley*[1] had acid values ranging from 4·8 to 12; the amounts of unsaponifiable matter varied from 1·45 to 1·66 per cent. One sample yielded 0·79 per cent arachidic acid of the melting point 70·4° C.

Ravison oil has a higher iodine value and exhibits stronger drying properties than rape oil. It is therefore not so suitable for lubricating purposes as rape oil, and its admixture with (or substitution for) rape oil must be looked upon as adulteration.

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[1] *Lubrication and Lubricants*, p. 106.

[TABLE

Physical and Chemical Constants of Ravison Oil

<table>
<tr><th colspan="3">Specific Gravity.</th><th colspan="2">Solidifying Point.</th><th colspan="2">Saponification Value.</th><th colspan="2">Iodine Value.</th><th colspan="2">Maumené Test.</th><th colspan="3">Refractive Index. Oleo-refractometer.</th><th colspan="2">Viscosity. Redwood's Viscosimeter.</th></tr>
<tr><th>°C.</th><th></th><th>Observer.</th><th>°C.</th><th>Observer.</th><th>Mgrms. KOH.</th><th>Observer.</th><th>Per Cent.</th><th>Observer.</th><th>°C.</th><th>Observer.</th><th colspan="2">" Degrees."</th><th>Observer.</th><th></th><th>Observer.</th></tr>
<tr><td>15</td><td>0·9175-0·921</td><td>Cloëz</td><td>-8</td><td>Jean</td><td>174</td><td>Jean</td><td>105</td><td>Jean</td><td>45[1]</td><td>Jean</td><td colspan="2">+25</td><td>Jean</td><td>about 6 to 13 per cent lower than refined Rape Oil</td><td>Archbutt and Deeley</td></tr>
<tr><td>,,</td><td>0·918-0·920</td><td>Itallie</td><td></td><td></td><td>177·9-179·3</td><td>Archbutt and Deeley</td><td>108·9-121·7</td><td>Archbutt and Deeley</td><td>65·8-76</td><td>Archbutt and Deeley</td><td colspan="2">+18[2]</td><td>,,</td><td></td><td></td></tr>
<tr><td>15·5</td><td>0·9183-0·9217</td><td>Archbutt and Deeley</td><td></td><td></td><td></td><td></td><td>101·4</td><td>Tortelli and Ruggeri</td><td></td><td></td><td colspan="2">+16 to +20</td><td>Pearmain.</td><td></td><td></td></tr>
<tr><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td colspan="3">Butyro-refractometer.</td><td></td><td></td></tr>
<tr><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>At °C.</td><td>Degrees.</td><td>Observer.</td><td></td><td></td></tr>
<tr><td>,,</td><td>0·9179</td><td>Lewkowitsch</td><td></td><td></td><td>177·2</td><td>Lewkowitsch</td><td>117·4</td><td>Lewkowitsch</td><td></td><td></td><td>20
25</td><td>74
71·5</td><td>Lewkowitsch</td><td>334-352 seconds at 70° F.</td><td>Lewkowitsch</td></tr>
</table>

Physical and Chemical Constants of the Mixed Fatty Acids

<table>
<tr><th colspan="3">Specific Gravity.</th><th colspan="2">Iodine Value.</th></tr>
<tr><th>°C.</th><th></th><th>Observer.</th><th>Per cent.</th><th>Observer.</th></tr>
<tr><td>100</td><td>0·8802</td><td>Archbutt and Deeley</td><td>126·1[3]</td><td>Archbutt and Deeley</td></tr>
<tr><td></td><td></td><td></td><td colspan="2">Iodine Value of Liquid Fatty Acids.</td></tr>
<tr><td></td><td></td><td></td><td>124·2</td><td>Tortelli and Ruggeri</td></tr>
</table>

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[1] By Jean's thermelaeometer.

[2] Italian Ravison.

[3] Iodine value of the oil 121·7.

HEDGE MUSTARD OIL[1]

French—*Huile de raphanistre.* German—*Hederichoel.*
Italian—*Olio di rafano.*

Physical and Chemical Constants of Hedge Mustard Oil

Specific Gravity at 15° C.	Solidifying Point °C.	Saponification Value. Mgrms. KOH.	Iodine Value. Per cent.
0·9175	−8	174	105 (Hübl)

This oil is obtained from the seeds of the common hedge radish (runch, wild radish), *Raphanus Raphanistrum.* The seeds contain 35-40 per cent of oil. It possesses a characteristic taste.

Hedge mustard oil also closely resembles rape oil. It was expressed for the first time in 1880, with a view to substituting it for rape oil. It is detected in rape oil, according to *Valenta*, by treating 5 grms. of the sample with an amount of alcoholic potash, which is insufficient for complete saponification, filtering the soap solution from the unsaponified oil, and adding strong hydrochloric acid to the filtrate, when a green colour is said to indicate the presence of hedge mustard oil.

RAPE OIL [COLZA OIL]

French—*Huile de colza.* German—*Rüboel.*
Italian—*Olio di colza.*

For tables of constants see pp. 561-563.

The various kinds of rape oil are obtained from the seeds of *Brassica campestris* and of several largely cultivated varieties of this species belonging to the natural order *Cruciferæ.* The oils from these plants are, especially in this country, indiscriminately termed rape oil or colza oil; on the Continent, however, the last two names designate two different kinds of oil. Occasionally, also, three kinds are recognised under the following names:—

1. Colza oil (French—*Huile de colza;* German—*Kohlsaatoel;* Italian—*Olio di colza*) from the seeds of *Brassica campestris.*
2. Rape oil (French—*Huile de navette;* German—*Rapsoel, Repsoel*) from the seeds of *Brassica campestris*, var. *Napus.*
3. [Rubsen oil] French—*Huile de rabette;* German—*Rüboel, Rübsenoel;* from the seeds of *Brassica campestris*, var. *Rapa.*

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[1] Valenta, *Dingl. Polyt. Journ.* 247, 36.

A further distinction of a winter and a summer variety of each of these three oils may be indulged in, as has been done by some writers, but as it is impossible to distinguish these last-mentioned varieties by their chemical or physical characteristics, and furthermore as, in the trade, all three varieties are indiscriminately sold as *rape oil* or *colza oil*, I comprise within the two tables of the physical and chemical constants of the oil and its mixed fatty acids all the data that have been furnished by the several observers who have examined the rape oils of commerce. It is very desirable, however, that when constants of rape oil are published, full particulars as to variety and source be given. I therefore give, by way of example, the following table :—

[TABLE

Constants of Genuine Rape Oils (Crossley and Le Sueur)

Name.	Variety.	Source.	Specific Gravity at 15·5° C. (water 15·5=1).	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Hehner Value.	Refractive Index at 40° C.	Viscosity.		Acid Value.	Optical Activity in 200 mm. tube.
				Mgrms. KOH.	Per cent.	c.c. $\frac{1}{10}$ norm. KOH.	Per cent.	Butyro-refractometer.	Seconds at 70° F.	Compared with Water at 70° F.		
Brassica campestris	red	N.W. Provinces	0·9148	171·6	99·2	0·79	96·3	...	390·6	15·38	2·90	– 7′
,, ,,	glauca	,,	0·9142	171·4	97·7	0·67	95·04	59·2	402·6	15·85	1·78	– 10′
,, ,,	dichotoma	,,	0·9154	172·2	104·8	0·22	95·57	...	371·8	14·64	1·57	...
,, ,,	...	Punjab	0·9163	173·4	96·25	0·43	94·56	...	393·2	15·48	2·57	...
,, ,,	brown	Bombay	0·9171	172·8	94·1	0·00	...	...	464·6	18·29	4·00	...
,, ,,	yellow	,,	0·9141	169·4	96·66	0·00	...	...	413·8	16·29	1·42	– 5′
,, napus	...	Bengal	0·9146	167·7	97·7	0·00	95·55	58·8	398·0	15·67	3·77	– 15′
Eruca sativa	allied to mustard	Bombay	0·9177	170·4	99·72	0·66	95·49	...	371·0	14·61	2·10	...
,, ,,	,, ,,	Punjab	0·9152	169·0	97·41	0·11	...	...	405·8	15·98	3·70	– 11′
,, ,,	,, ,,	Cawnpore	0·9165	174·1	99·10	0·77	...	...	369·4	14·54	2·51	– 18′

Physical and Chemical Constants of Rape Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Reichert Value.	
At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.
15	0·914-0·917	Allen	−4 to −6	Girard	178·7	Köttstorfer	100·8-102·4	Archbutt	0·25	Reichert
,,	0·9142	Souchère[1]	0	Holde	177	Valenta	97·8[4]	,,	0·3-0·4	Medicus and Scherer
,,	0·9151	,, [2]			175-179	Allen	99·1-105·6	Thomson and Ballantyne		
,,	0·9150-0·917	De Negri and Fabris[1]			170-176·4	Archbutt[3]			0·0-0·79	Crossley and Le Sueur[2]
15·5	0·9133-0·9168	Thomson and Ballantyne			175[4]	,,	97·65-102·1	De Negri and Fabris		
,,	0·9132-0·9159	Archbutt[3]			170·6-175·3	Thomson and Ballantyne	94·1-104·8	Crossley and Le Sueur[5]		
15·5 (water 15·5=1)	0·9141-0·9177	Crossley and Le Sueur[5]			175-177	De Negri and Fabris	98-103·6	Lewkowitsch[6]		
23	0·910	Dieterich			177-178	Oliveri				
99 (water 15·5=1)	0·8632	Allen			171·7-176·5	Lewkowitsch[6]				
					167·7-173·4	Crossley and Le Sueur[5]				

[1] Colza oil.

[2] Rape oil.

[3] Fifty-two samples. *Journ. Soc. Chem. Ind.* 1886, 310.

[4] From Guzerat seed.

[5] Indian Oils, cp. p. 560.

[6] Commercial rape oils of good quality.

Physical and Chemical Constants of Rape Oil—continued.

<table>
<tr><th colspan="2" rowspan="2">Hehner Value.</th><th colspan="4">Thermal Tests.</th><th colspan="3" rowspan="2">Refractive Index.</th><th colspan="2" rowspan="2">Viscosity (Redwood's Viscosimeter).</th></tr>
<tr><th colspan="2">Maumené Test.</th><th colspan="2">Heat of Bromination.</th></tr>
<tr><th>Per cent.</th><th>Observer.</th><th>°C.</th><th>Observer.</th><th>°C.</th><th>Observer.</th><th>At °C.</th><th></th><th>Observer.</th><th>Seconds at 70° F.</th><th>Observer.</th></tr>
<tr><td rowspan="7">95·1
94·56-96·3</td><td rowspan="7">Bensemann
Crossley and Le Sueur[1]</td><td>55-64
51-60
49-51</td><td>Archbutt
Allen
De Negri and Fabris</td><td rowspan="7">18·4
17·6
17·3
17-20·3</td><td rowspan="7">Hehner and Mitchell
Jenkins
Archbutt</td><td>15
20
60</td><td>1·4720 to 1·4757
1·4735
1·4667</td><td>Strohmer
Holde
Thoerner</td><td rowspan="7">370-380
369·4-464·6</td><td rowspan="7">Lewkowitsch
Crossley and Le Sueur</td></tr>
<tr><td colspan="2">Specific Temperature Reaction.</td><td colspan="3">Oleo-refractometer.</td></tr>
<tr><td rowspan="5">125-144</td><td rowspan="5">Thomson and Ballantyne</td><td colspan="2">"Degrees" at 22° C.</td><td>Observer.</td></tr>
<tr><td colspan="2">+15 to +18·5
+16 to +20</td><td>Jean
Pearmain</td></tr>
<tr><td colspan="3">Butyro-refractometer.</td></tr>
<tr><td>At °C.</td><td>"Degrees."</td><td>Observer.</td></tr>
<tr><td>25
40</td><td>68
58·8-59·2</td><td>Mansfeld
Crossley and Le Sueur[1]</td></tr>
</table>

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[1] Indian Oils, cp. p. 560.

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.			Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.		Refractive Index.	
°C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.	At 60° C.	Observer.
99 (water 15·5=1)	0·8438	Allen	18·5	Allen	18·3-19·5	Allen	185	Thoerner	321·2	Allen	96·3-99·02	Morawski and Demski	1·4991	Thoerner
100 (water 100=1)	0·8758	Archbutt	18-17	Bensemann[3]	21-22	Bensemann[4]			307	Williams	105·6	Williams		
					18·5-21	Archbutt			314	Valenta	99·8-103·1	De Negri and Fabris		
					16-19	De Negri and Fabris					103·6[5]	Wijs		
			16	Thoerner	20	Thoerner					Iodine value of the liquid fatty acids.			
			Titer Test.								120·7	Wallenstein and Finck		
			12·7-13·6[1]	Lewkowitsch							124·2-125·5[6] 114·3[7]	Tortelli and Ruggeri		
			11·7-12·2[2]	,,										

[1] Colza oil.
[2] Rape oil.
[3] Point of incipient fusion.
[4] Point of complete fusion.
[5] Cold pressed.
[6] Iodine Value 102·2-101·7.
[7] Very old sample, iodine value=96·4.

For further numbers cp. pp. 561-563.

Rape seed is crushed between rollers and the meal is either expressed or extracted with carbon bisulphide or petroleum ether. The extracted oil is, as a rule, purer than the expressed oil, since a considerable amount of mucilaginous matter passes into the oil when the seed is expressed. The cakes obtained by expression form an excellent cattle food, if the seed has been tolerably pure, *i.e.* free from mustard seed and wild seeds. The extracted meal is unsuitable as cattle food, and is chiefly used as manure, at any rate in this country, although some meal, especially on the continent, finds its way into compound cakes.

Rape seed contains from 33 to 43 per cent of oil.

The crude oil is dark in colour, and before being put on the market it is refined by treatment with about one per cent of strong sulphuric acid, which coagulates and carries down the impurities. The settled oil is then washed with water until free from mineral acid.

The refined oil of commerce is pale yellow, and possesses a characteristic smell [which may serve to identify the oil], and an unpleasant, harsh taste. 100 parts of alcohol dissolve 0·534 parts of the oil.

Glycerides of the saturated fatty acids occur in rape oil to a small amount only. *Tolman* and *Munson* found by the lead-salt-ether method 1·02 per cent (and less), of solid fatty acids. What *Reimer* and *Will*[1] termed behenic acid in rape oil has been shown by *Ponzio*[2] to be in reality crude arachidic acid (*i.e.* a mixture of arachidic acid and lignoceric acid). *Archbutt*[3] confirmed the occurrence of "arachidic acid" in a number of commercial rape oils. His observations are reproduced in the following table:—

Origin of Oil.	Crude Arachidic Acid.	
	Per Cent.	Melting Point °C.
Crude, several years old, from Rubsen	0·59	69·2
Crude, several years old, from Raps	0·36	69·0
Kustendje (Black Sea)	0·84	70·4
Refined, Stettin	1·14	69·0
	after purification by one recrystallisation from 90 per cent alcohol	
	0·91	72·2
Oil prepared in the Laboratory from Guzerat seed	1·61	71·1
	after purification by twice recrystallising from 50 c.c. of 90 per cent alcohol	
	1·43	73·1

Amongst the unsaturated fatty acids, erucic and rapic acids have been identified. Since the iodine value of the unsaturated liquid fatty acids lies in the neighbourhood of 120, whereas the

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[1] *Berichte*, 1887, 2388.

[2] *Journ. prakt. Chemie*, 1893 [48], 487; *Journ. Soc. Chem. Ind.* 1894, 257.

[3] *Journ. Soc. Chem. Ind.* 1898, 1009.

respective iodine values of rapic and erucic acids are 90·07 and 85·81, the presence of unsaturated fatty acids belonging to the linolic, or to the linolenic series must be suspected. Indeed *Hehner* and *Mitchell* obtained 3·6 per cent of a brominated acid melting at 179° C.; the same compound was also isolated by *Farnsteiner* and by *Walker* and *Warburton*; the last named observers obtained 2·4 to 3·4 per cent of linolenic hexabromide.

On standing, "stearine" separates from rape oil at the ordinary temperature. *Halenke* and *Möslinger*[1] examined a specimen of rape "stearine" with the following result:—

	Melting Point. °C.	Saponification Value.
Fat	38·5	161·76
Fatty acids . .	34	160·05

It follows from these numbers that the "stearine" consisted of almost pure trierucin.

Reimer and *Will*[2] however, found that a specimen of rape oil "stearine" consisted of dierucin. By dissolving the solid mass in ether, filtering and precipitating with alcohol, colourless needles having the melting point 47° C. were obtained.

The unsaponifiable matter—phytosterol—contained in rape oil, varies from 0·5 to 1 per cent. This figure is rarely exceeded. Rape oils containing larger amounts of unsaponifiable matter, exceeding say 2 per cent, should be looked upon with suspicion.

Commercial rape oil contains as a rule free fatty acids. In view of the importance which the proportion of free fatty acids has on the valuation of commercial rape oils intended for lubricating purposes and for burning, I collate in the following table some numbers found by various observers:—

Free Fatty Acids in Rape Oils

Description of Oil.	No. of Samples.	Free Fatty Acids in terms of Oleic Acid.	Observer.
		Per cent.	
...	1	4·28	Salkowski
...	1	6·64	Rechenberg
Sweet oil	3	0·53–1·82	Nördlinger
Commercial oil, expressed .	9	0·52–6·26	,,
,, ,, extracted .	2	0·77–1·1	,,
,, ,, . . .	5	2·43–6·24	Thomson and Ballantyne
,, ,, . . .	50	1·7–5·5	Archbutt
,, ,, . . .	5	1·05–3·9	Deering
Indian oils . . .	10	0·7–2·01	Crossley and Le Sueur

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[1] *Corresp. d. Vereins d. bayer. Chem.* No. 1.

[2] *Berichte*, 1886, 332.

In *Livache's* test rape oil absorbs 2·9 per cent of oxygen after seven days, whereas the fatty acids absorb only 0·9 per cent after eight days. The oil thickens and becomes rancid, without, however, drying. Rape oil may, therefore, be considered as representing a class of oils occupying an intermediate position between the semi-drying and the non-drying oils.

It is most likely due to this slight drying power that old rape oil samples exhibit notable acetyl numbers. Thus *Lewkowitsch* found in a sample of old colza oil the acetyl value 14·7, and *Gripper* values varying from 24 to 41·7.

The following table, due to *Gripper*,[1] gives the characteristics of a number of old rape oils which had been standing in corked bottles in full daylight for the times stated. For comparison, the numbers obtained for fresh rape oil are added. It appears that air must have had access to the oil, as the specific gravities and viscosities, as also the acetyl numbers and soluble fatty acids, had increased, whilst the iodine values had decreased.

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[1] *Journ. Soc. Chem. Ind.* 1899, 342.

	Specific Gravity at 60° F.	Free Fatty Acids as Oleic Acid. Per Cent.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Hehner Value.	Soluble Fatty Acids, equivalent to Per Cent KOH.	Viscosity at 60° F. Rape Oil at 60° F. =100.	Insoluble Fatty Acids.			
									Melting Point. °C.[1]	Molecular Weight.	Iodine Value.	Acetyl Value.
Rape oil, 8 years 9 months old	0·9356	13·35	197·2	63·89	20·2	89·1	3·48	1163	21·1	326·1	72·07	41·73
,, ,, 6 ,, 6 ,, ,,	0·9478	8·19	195·7	70·83	...	90·34	...	750 (about)	16·7	320·0	...	...
,, ,, 7 ,, 5 ,, ,,	0·9441	7·98	194·3	72·06	15·7	90·17	2·80	587	18·1	320·0	79·06	38·78
,, ,, 7 ,, 10 ,, ,,	0·9414	11·04	188·4	71·52	...	89·91	2·47	515	17·2	320·0	77·28	35·39
,, ,, 9 ,, 1 ,, ,,	0·9265	6·76	180·9	83·37	...	92·90	1·63	214	20·0	324·6	86·02	28·72
,, ,, 10 ,, 1 ,, ,,	0·9287	8·38	180·6	90·38	...	92·67	1·51	245	18·3	314·4	...	...
,, ,, 4 ,, 8 ,, ,,	0·9196	4·22	179·4	94·35	...	94·34	1·12	145	18·1	320·5	98·23	...
,, ,, 8 ,, 2 ,, ,,	0·9197	5·62	181·7	98·90	...	94·07	0·95	131	16·1	320·5	103·93	25·71
,, ,, 9 ,, 8 ,, ,,	0·9156	4·82	176·7	98·64	...	95·04	0·67	115	17·8	329·0	...	...
,, ,, 4 ,, 0 ,, ,,	0·9142	4·30	178·0	96·92	4·2	95·70	0·67	110	18·3	320·5	...	...
,, ,, 6 ,, 0 ,, ,,	0·9170	5·74	180·4	101·34	...	96·00	0·78	104	17·2	324·6	107·12	28·94
,, ,, 5 ,, 2 ,, ,,	0·9167	4·32	178·6	100·35	...	95·70	0·69	102	19·1	320·5	104·17	24·45
Rape oil, fresh . . .	0·9140	2·70	177·8	99·08	...	95·60	0·39	100	20	...	...	23·11

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[1] Determined by the Crossley and Le Sueur's method.

The **elaïdin test** does not give characteristic indications.

Rape oil is largely adulterated with the following fatty oils: Linseed, hemp seed, poppy seed, cameline, cotton seed, ravison, and hedge mustard oils, and refined fish and blubber oils. Paraffin and rosin oils are also frequently added fraudulently.

In order to "correct" the specific gravity, which may have been raised by the addition of the latter two oils, sperm oil is also added. The unsaponifiable paraffin and rosin oils are easily detected by estimating the amount of *unsaponifiable matter.* The presence of sperm oil also increases the amount of unsaponifiable matter, since sperm oil contains 37 to 41 per cent of unsaponifiable substances. Hence, the examination of the unsaponifiable matter for the presence of sperm oil alcohols may become necessary in special cases. (Cp. chap. ix.)

The addition of large quantities of linseed, hemp seed, poppy seed, cameline, fish and blubber oils will be readily recognised by the iodine value, and chiefly by the determination of one of the following characteristics: specific gravity, melting point of the fatty acids, thermal tests, saponification value, and also the viscosity of the oil.

The **specific gravity** of rape oil rarely exceeds 0·916, and this may be considered for practical purposes as the limit, although, as will be seen from the table given above, higher values have been recorded. Of fifty-two samples examined by *Archbutt*—

7 samples had a specific gravity below 0·9140
27 ,, ,, ,, above 0·9139 but below 0·9150
18 ,, ,, ,, ,, 0·9149 ,, 0·9160

The specific gravities of the other fatty oils that may be used as adulterants being higher than 0·9160, a sample of oil the specific gravity of which exceeds that figure must be looked upon with suspicion. Of course, presence of an unsaponifiable oil cannot be detected by determination of the specific gravity alone; it has been pointed out already that the specific gravity of an adulterated oil is usually "corrected."

The **melting point of the fatty acids** and the **solidifying point** (titer test), will be higher than the normal one if cotton seed oil has been added; on the other hand, it will be lowered by the presence of linseed oil or of any of the other oils mentioned above. If cotton seed oil be suspected the *Halphen* colour reaction may be used as a confirmatory test. In case heated cotton seed oil had been used, this test will fail. The nitric acid colour test is too uncertain in the presence of rape oil.

The **thermal test** with sulphuric acid or bromine[1] is still largely used, although the indications furnished by the iodine value are much more reliable. The thermal reactions will indicate admixture of linseed or other drying oils, or semi-drying oils, such as cotton seed oil.

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[1] Cp. Archbutt, *Journ. Soc. Chem. Ind.* 1897, 311.

The **saponification value** of the sample under examination will easily lead to a decision whether any other fatty oil, with *the exception of an oil belonging to the rape oil group, such as ravison or hedge mustard oil*, is present. In consequence of the large proportion of erucin in rape oil its saponification value is very low, lower than that of any of the fatty oils mentioned above. [Castor oil, which is also characterised by a low saponification value, would be detected by the specific gravity and acetyl value.] It should, however, not be forgotten that a low saponification value will also be found if unsaponifiable oils are present. If so, they must be first separated, and the neutralisation value of the fatty acids determined subsequently.

The following are the saponification values of the fifty-two samples of rape oil examined by *Archbutt*:—

4	samples	170 to 171
12	,,	171 ,, 172
9	,,	172 ,, 173
14	,,	173 ,, 174
11	,,	174 ,, 175
1	,,	175 ,, 176
1	,,	176 ,, 177

It may be repeated that the other members of the rape oil class also have low saponification values.

The determination of the **viscosity** of rape oil is a very valuable means of ascertaining its purity. It will be found best to compare the sample with a standard rape oil of known purity, as the viscosity of rape oil is fairly constant. Since no other oil, with the exception of castor oil, likely to be used as an adulterant possesses so high a viscosity as rape oil, the genuineness of the sample can thus be ascertained.

The **Valenta test** is very characteristic of rape oil, and will prove useful as an additional means of deciding whether a sample of rape oil is genuine or not.

Fish oils and **blubber oils** in rape oil may be recognised by their peculiar smell and taste, especially on warming, and also by the intensity of the phospho-molybdic acid reaction. More important evidence will be furnished by the determination and examination of the hexabromide prepared from the mixed fatty acids. Undoubted evidence will be furnished by the phytosteryl acetate test (cp. Linseed Oil, p. 462), as also by the iodine value of the oil and of its liquid fatty acids.

Since rape oil is refined with concentrated sulphuric acid, commercial oils should be tested for the presence of sulphuric acid by shaking the oil with warm water and examining the aqueous layer.

The detection of rape oil in *other oils* by means of colour reactions (such as *Mailho's* or *Schneider's* reagents), purporting to show presence of sulphur, can no longer be considered as useful, since it has been proved that sulphur is not a constitutive element of the oils obtained from the seeds of *Cruciferæ*. The "cold-drawn" oils of commerce are completely devoid of sulphur, but oils extracted by means of carbon bisulphide may retain some sulphur, it being difficult to remove the last traces of the solvent. The colour reaction proposed recently by *Palas*[1] for the detection of rape oil in olive oil (viz. agitation with rosaniline sulphite) is valueless, as experiments instituted by the writer have shown.

Rape oil in other oils will be detected by its characteristic smell, and by the influence it exercises on the constants of the oil under examination, such as the iodine value of the oil, the iodine value of the liquid fatty acids, and chiefly on the saponification value.

The "cold-drawn" oil is used as an edible oil, especially in India. Enormous quantities of the oil are used for lubricating purposes. Smaller quantities are used on the Continent for the making of soft soap. Rape oil still finds large employment on railways as a burning oil.

Charlock oil, from the seeds of *Sinapis arvensis*, wild mustard charlock, frequently contaminates rape oil.

The oil itself is not a commercial article, since the endeavour of the rape seed growers is to destroy the charlock plant as being a weed.

BLACK MUSTARD SEED OIL

French—*Huile de moutarde noire*. German—*Schwarzsenfoel*.
Italian—*Olio di mostarda nera*.

For table of constants see p. 572-573.

Black mustard seed oil is obtained from the seeds of *Sinapis nigra* (*Brassica nigra*). The seeds contain 31-33 per cent of oil. The oil has a brownish-yellow colour, and possesses a mild taste; it smells of the ethereal mustard oil.

In its chemical composition it closely resembles rape oil. *Tolman* and *Munson* obtained from various samples by the lead-salt-ether method from 2·32-4·05 per cent of solid fatty acids. Amongst these occurs arachidic acid; amongst the unsaturated acids erucic and a liquid fatty acid[2] (rapic acid ?) have been found.

Nördlinger found in two samples of the oil free fatty acids to the extent of 0·68 and 1·02 per cent, calculated to oleic acid.

The oil is obtained as a by-product in the manufacture of ethereal mustard oil. It is not suitable for burning; it is, therefore, used for soap-making.

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[1] *Journ. Soc. Chem. Ind.* 1897, 361.

[2] Goldschmiedt, *Wiener Berichte*, 70 [2], 451.

The oil from Indian mustard seed, *Brassica* (*Sinapis*) *juncea* (a variety of *Sinapis nigra*), has been examined by *Crossley* and *Le Sueur*.[1] The following characteristics were ascertained :—

Origin.	Specific Gravity at 15·5° (water 15·5°=1).	Saponification Value. Mgrms. KOH.	Iodine Value. Per cent.	Reichert-Meissl Value. c.c. $\frac{1}{10}$ norm. KOH.	Hehner Value. Per cent.	Refractive Index. Butyro-refractometer at 40° C.	Viscosity in Redwood's Viscometer. Seconds at 70° F.
Bombay	0·9206	180·1	108·29	0·89	—		382·8
Bengal, var. rai.	0·9158	172·1	101·82	0·33	95·49	60	379·3

The optical activity in a 200 mm. tube was –0° 25′ and –0° 18′ respectively.

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[1] *Journ. Soc. Chem. Ind.* 1898, 991.

Physical and Chemical Constants of Black Mustard Seed Oil

Origin.	Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Hehner Value.	
	At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	Per cent.	Observer.
	15	0·916-0·920	Allen	−17·5	Chateau	174·0-174·6	De Negri and Fabris	96	Moore	95·05	Crossley and Le Sueur
	15	0·9170-0·9175	De Negri and Fabris			174·7	Blasdale	106·25- 106·57	De Negri and Fabris		
	15	0·9161	Blasdale			175·8	Wijs	103·07	Lengfeld and Paparelli		
Bengal	15·5 (water 15·5 = 1)	0·9155	Crossley and Le Sueur[2]			173·3	Crossley and Le Sueur	103·6	Blasdale[1]		
Central Provinces		0·9185	,,			173	,,	105·8-113	Tolman and Munson		
	,,	0·9170-0·9193	Tolman and Munson					122·3	Wijs		
India	20	0·9143	Wijs					98·84	Crossley and Le Sueur		
								110·51	,,		

Physical and Chemical Constants of Black Mustard Seed Oil—continued

Maumené Test.		Refractive Index.			Viscosity.	
°C.	Observer.	At °C.		Observer.	Seconds at 70° F.	Observer.
44	Girard	15·5	1·4672	Tolman and Munson	425·4	Crossley and Le Sueur
42-43	De Negri and Fabris	Butyro-refractometer.			355·4	,,
58·5 (!)	Lengfeld and Paparelli	15·5	76·5	Tolman and Munson		
			59·5	Crossley and Le Sueur		

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[1] *Journ. Soc. Chem. Ind.* 1896, 206.

[2] *Journ. Soc. Chem. Ind.* 1898, 991. The two samples had the acid values 7·35 and 5·72 respectively, and the optical activity, in a 200 m.m. tube, 0° 17′ and 0° 30′ respectively.

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.		Neutralisation Value.		Mean Molecular Weight.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.	Mgrms. KOH.	Observer.		Observer.
15·5	Girard	16	Girard	109·6	De Negri and Fabris	187·1	Wijs	299·8	Wijs
		16-17	De Negri and Fabris						
		15	Blasdale	126·5	Wijs				
				Liquid Fatty Acids.					
				119·8	Tolman and Munson				

WHITE MUSTARD SEED OIL

French—*Huile de moutarde blanche.* German—*Weissenfoel.*
Italian—*Olio di mostarda bianca.*

For tables of constants see pp. 575, 576.

White mustard seed oil is obtained from the seeds of *Sinapis alba* (*Brassica alba*). The seeds contain 25-26 per cent of oil. The oil is of a golden-yellow colour, and has a burning taste.

Most of the physical and chemical constants are almost identical with those of black mustard oil. The iodine values, however, appear to differ considerably. This agrees with *Tolman* and *Munson's* statement that white mustard seed oil yields only traces of solid acids by the lead-salt-ether method. *Hehner* and *Mitchell* obtained 1·5 per cent of linolenic hexabromide from a specimen of white mustard seed oil.

A sample examined by *Archbutt*[1] yielded 1·18 per cent of crude arachidic acid, melting point 69° C.

The oil is used as a burning and lubricating oil.

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[1] *Journ. Soc. Chem. Ind.* 1898, 1009.

[Table

Physical and Chemical Constants of White Mustard Seed Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Hehner Value.	
°C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	Per cent.	Observer.
15	0·9125-0·9160	De Negri and Fabris	−16·3	Chateau	170·3-171·4	De Negri and Fabris	92·1-93·8	De Negri and Fabris	96·7	Lengfeld and Paparelli
15	0·9151	Blasdale			173·9	Blasdale	97·68	Lengfeld and Paparelli	95·86	Crossley and Le Sueur
15·5	0·914-0·916	Allen			171·2	Crossley and Le Sueur	98·4	Blasdale		
15·5 (water 15·5=1)	0·9142[1]	Crossley and Le Sueur			174·6	Wijs	96·75	Crossley and Le Sueur		
20	0·9121	Wijs					103	Wijs		

Physical and Chemical Constants of White Mustard Seed Oil—continued

Maumené Test.		Refractive Index.			Viscosity.	
°C.	Observer.	°C.		Observer.	Seconds at 70° F.	Observer.
44·45	De Negri and Fabris	15·5	1·4750	Tolman and Munson	402	Crossley and Le Sueur
49·5	Lengfeld and Paparelli	Butyro-refractometer.				
		15·5	74·5	Tolman and Munson		
		40	58·5	Crossley and Le Sueur		

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[1] Indian oil (*Journ. Soc. Chem. Ind.* 1898, 991); the acid value of this specimen was 5·40; its optical activity in a 200 mm. tube −0° 9′.

Physical and Chemical Constants of the Mixed Fatty Acids

Melting Point. °C.	Iodine Value. Per cent.	Observer.	Neutralisation Value.		Mean Molecular Weight.	
			Mgrms. KOH.	Observer.		Observer.
15-16	94·7-95·87	De Negri and Fabris	185·8	Wijs	301·9	Wijs
		Blasdale				
16	106·2	Wijs				
	Liquid Fatty Acids.					
	103·1	Tolman and Munson				

RADISH SEED OIL

French—*Huile de raifort.* German—*Rettigoel.*
Italian—*Olio di ravano* (*ravanello*).

Radish seed oil, like the oils described last, closely resembles rape oil. The oil is obtained from the seeds of *Raphanus sativus* (rat-tail radish), which contain from 45-50 per cent of oil. The green colour said to be characteristic of the soap solution of hedge mustard oil is not noticeable on saponifying the oil (*De Negri* and *Fabris*).

An Indian oil from Assam had the acid value 14·5 (*Crossley* and *Le Sueur*[1]). This specimen is described as a *non*-drying oil.

Physical and Chemical Constants of Radish Seed Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.	
At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.
15 water at 15=1	0·9175	De Negri and Fabris	−10 to −17·5	Schaedler	178·05	De Negri and Fabris	95·6-95·9	De Negri and Fabris	0·33	Crossley and Le Sueur
15·5 water at 15·5=1	0·9163	Crossley and Le Sueur			173·8	Crossley and Le Sueur	92·85	Crossley and Le Sueur		
20	0·9142	Wijs[2]			179·4	Wijs	112·4	Wijs		

Physical and Chemical Constants of Radish Seed Oil—continued

Hehner Value.		Maumené Test.		Refractive Index.		Viscosity.	
Per cent.	Observer.	°C.	Observer.	Butyro-refractometer at 40° C.	Observer.	Seconds at 70° F.	Observer.
95·94	Crossley and Le Sueur	51	De Negri and Fabris	57·5	Crossley and Le Sueur	385·3	Crossley and Le Sueur

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.		Neutralisation Number.		Mean Molecular Weight.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.	Mgrms. KOH.	Observer.		Observer
13-15	De Negri and Fabris	20	De Negri and Fabris	97·1	De Negri and Fabris	189·5	Wijs	296	Wijs
				115·3	Wijs				

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[1] *Journ. Soc. Chem. Ind.* 1898, 991.

[2] *Zeits. Unters. Nahrungs u. Genussm.* 1903, 492.

JAMBA OIL [1]

French—*Huile de Jamba.* German—*Jambaoel.*
Italian—*Olio di Jambo.*

Physical and Chemical Constants of Jamba Oil

Specific Gravity.	Solidifying Point.	Saponification Value.	Iodine Value.	Hehner Value.	Maumené Test.	
15° C.	°C.			Per cent.	°C.	Observer.
0·9150-0·9158	−10 to −12	172·26	95·2-95·6	96·52	51-53	De Negri and Fabris
0·9151		174·8	102·5			Lewkowitsch

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.	Melting Point.	Neutralisation Value.	Iodine Value.	Mean Molecular Weight.	
°C.	°C.	Mgrms. KOH.	Per cent.		Observer.
16-11	19-21	173·8-174	96·1-96·2		De Negri and Fabris
				305	Lewkowitsch

This oil, obtained from the seeds of a plant belonging to a variety of the genus *Brassica*, is closely related to rape oil. It behaves somewhat abnormally in that it does not lend itself readily to the manufacture of "blown" oil, as the specific gravity of the oil does not rise by "blowing" at the same rate as that of other oils belonging to the rape oil group. A further instance of its abnormal behaviour is that the temperature does not rise spontaneously when the source of heat has been removed.

The sample examined in the writer's laboratory contained 0·45 per cent unsaponifiable matter; it yielded 1·05 per cent of fatty acids insoluble in petroleum ether.

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[1] De Negri and Fabris, *Annali del Laboratorio delle Gabelle*, 1891-92, 137.

(3) NON-DRYING OILS

The oils belonging to this class are characterised by lower iodine values than those of the two preceding classes. Linolenic acid appears to be completely absent; linolic acid seems to be present in small quantities only. Those oils which stand at the head of the list appear to still possess slight drying properties. Owing to the predominance of olein the non-drying oils solidify on treatment with nitrous acid, yielding hard elaïdin; castor oil gives in this test solid ricinelaïdin.

It should be noted that the oils are non-drying at the ordinary temperature only; at higher temperatures they become viscous and thicken. The chemical changes then taking place have not yet been investigated.

I have placed castor oil (and also grape seed oil, which seems to be related to it) at the end of this class, on account of its being a most markedly non-drying oil. The chemical composition of castor oil (and pending further confirmation also of grape seed oil) totally differs from that of all other fatty oils; so that for this reason the forming of a separate group, consisting of castor oil and grape seed oil, appears to be justified.

SMALL FENNEL OIL

French—*Huile de nigelle.* German—*Schwarzkümmeloel.*
Italian—*Olio di cominella (nigella).*

Physical and Chemical Constants of Small Fennel Oil.

Specific Gravity.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Hehner Value.	Refractive Index.
At 15·5° C. (water at 15·5 =1).	Mgrms. KOH.	Per cent.	c.c. $\frac{1}{10}$ norm. KOH.	Per cent.	Butyro-refractometer at 40° C.
0·9248	196·4	116·20	5·40	88·83	58·5

Small fennel oil is expressed in the East Indies from the seeds of *Nigella sativa*, and serves as an edible oil.

The sample examined by *Crossley* and *Le Sueur* had an acid value of 97·4; this very high acidity may explain the apparently abnormal *Hehner* and *Reichert-Meissl* values.

According to experiments made by *Crossley* and *Le Sueur* the oil is a non-drying oil.

QUINCE OIL

French—*Huile de coing.* German—*Quittensamenoel.*
Italian—*Olio di cotogno.*

The seeds of the quince, *Cydonia vulgaris*, contain about 15 per cent of a fatty oil of yellow colour, and pleasant odour faintly resembling that of almond oil.[1] The acid value of the specimen examined was 31·7.

The oil contains a liquid hydroxy acid, $C_{17}H_{32}(OH)CO_2H$, the dibromide of which melts at 108° C (p. 365). The solid acids contain myristic acid and another solid acid, which has not been identified hitherto.

Physical and Chemical Constants of Quince Oil

Specific Gravity.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Hehner Value.	Refractive Index.
At 15° C.	Mgrms. KOH.	Per cent.	c.c. $\frac{1}{10}$ norm. KOH.	Per cent.	Temperature.[2]
0·922	181·75	113	0·5	95·2	1·47292

CHERRY KERNEL OIL

French—*Huile de cerisier.* German—*Kirschkernoel.*
Italian—*Olio di ciliegie.*

For tables of constants see p. 581.

The constants given in the tables refer to extracted oil.

Cherry kernel oil is obtained from the kernels of the cherry (*Prunus cerasus*). The kernels contain 35-36 per cent of oil. The oil, when fresh, has a golden-yellow colour and a faint odour of almonds, which it loses when it turns rancid.

With nitric acid of specific gravity 1·4 cherry kernel oil becomes dark reddish brown; with *Bieber's* reagent (p. 593) a brown colouration is obtained.

De Negri and *Fabris* found a notable quantity of hydrocyanic acid in the extracted oil.

In South Germany (Würtemberg) the "cold-drawn" oil is used as an edible oil; the oil expressed at a higher temperature serves as a burning oil, and also for soap-making. As cherry kernel oil easily turns rancid, it is not used to adulterate almond oil.

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[1] Herrmann, *Arch. d. Pharm.* 1899, 237, 358.

[2] Temperature not stated.

Physical and Chemical Constants of Cherry Kernel Oil

Specific Gravity.		Solidifying Point.		Saponification Value		Iodine Value.		Maumené Test.	
At 15° C.	Observer.	°C	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C	Observer.
0·9235-0·9238	De Negri and Fabris	−19 to −20	De Negri and Fabris	194·8-195	De Negri and Fabris	110·8-110·9	De Negri and Fabris	45	De Negri and Fabris
0·9285	Micko			193·4	Micko	114·3	Micko		
						113·2[1]	Tortelli and Ruggeri		

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.
15-13	De Negri and Fabris	19-21	De Negri and Fabris	189	Micko	296·2	Micko	114·3	De Negri and Fabris
...	...	16-20·6[2]	Micko	...	...	...	...	104·3	Micko
								Liquid Fatty Acids.	
								124·7	Tortelli and Ruggeri

[1] Cold pressed oil.

[2] Determined by the capillary tube method.

CHERRY LAUREL OIL[1]

French—*Huile de laurier cerise.* German—*Kirschlorbeeroel.*
Italian—*Olio di lauroceraso.*

Physical and Chemical Constants of Cherry Laurel Oil

Specific Gravity.	Solidifying Point.	Saponific. Value.	Iodine Value.	Maumené Test.
At 15° C.	°C.	Mgrms. KOH.	Per cent.	°C.
0·9230	−19 to −20	194	108·9	44·5

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.	Melting Point.	Iodine Value.
°C.	°C.	Per cent.
17-15	20-22	112·1

This oil has been extracted from the kernels of the cherry laurel (*Prunus laurocerasus*), a tree cultivated in Italy since the sixteenth century.

Cherry laurel oil has a golden-yellow colour; its odour resembles that of bitter almonds. This oil, like the preceding one, contains appreciable quantities of hydrocyanic acid.

APRICOT KERNEL OIL

French—*Huile d'abricotier.* German—*Aprikosenkernoel.*
Italian—*Olio di albicocche.*

For tables of constants see p. 584.

Apricot kernel oil is obtained from the kernels of the apricot (*Prunus Armeniaca*). The kernels contain from 40-45 per cent of oil.

The freshly expressed oil is almost colourless; on keeping it becomes yellow.

With nitric acid, spec. grav. 1·4, apricot kernel oil assumes an orange colour. With *Bieber's* reagent (p. 593) a peach-blossom colour

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[1] De Negri and Fabris, *Annali del Laboratorio Chimico delle Gabelle*, 1891-92, 173.

is obtained; this is so characteristic of the oil, that by means of this colour reaction apricot kernel oil is identified, and can be detected if present in almond oil in large quantities.

The deep red colouration obtained on shaking the oil with an ethereal solution of phloroglucinol (one-tenth per cent solution) is not so characteristic of the oil, since some almond oils (see p. 595) give the same colour reaction.[1] It should also be noted that the colour reaction is much stronger in the case of fresh oils than with samples that have been kept for half a year and longer.

A sample of oil (extracted) examined by *Micko* had the acid value 0·64. A three months' old sample examined by *Lewkowitsch* had the acid value 2·8.

Apricot kernel oil is used as an edible oil; in perfumery it is employed for adulterating or wholly substituting almond oil. Apricot kernel oil forms an important article of commerce. The commercial "almond oil, French," is practically pure apricot kernel oil, or a mixture of apricot kernel and peach kernel oils (cp. p. 587).

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[1] Lewkowitsch, *Analyst*, 1904, 106.

[TABLE

Physical and Chemical Constants of Apricot Kernel Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Hehner Value.		Maumené Test.		Refractive Index. Butyro-refractometer.		
At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.	At °C.	"Degrees."	Observer.
15	0·9191	Valenta	−20	Maben	192·2-192·9	De Negri and Fabris	101	De Negri and Fabris	0·00	Crossley and Le Sueur	95·40[1]	Crossley and Le Sueur	46	Girard	25	65·6	Beckurts and Seiler
15	0·9204	Maben											42·5	De Negri and Fabris			
15·5 (water at 15·5=1)	0·9195[1]	Crossley and Le Sueur			193·11	Micko	108	Micko							25	66·6	Mansfeld
					192·9	Valenta	96·02	Crossley and Le Sueur							40	57·5[1]	Crossley and Le Sueur
	0·9172[5] 0·9200[4]	Lewkowitsch			188[1]	Crossley and Le Sueur	104·2-104·7[3]	Tortelli and Ruggeri							40	58·0[4]	Lewkowitsch
90	0·901-0·9015	Dieterich			198·2[5]	Lewkowitsch									40	57·0[5]	,,
					190·3-192·4[4]	,,	100·1[4]	Wijs							50	52·25	Dieterich
							107·4-108·7[4]	Lewkowitsch									
							107·9	,,									

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.			Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.		Refractive Index. Butyro-refractometer.		
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.	At °C.	"Degrees."	Observer.
15	0·9195	Dieterich	0	Hübl	4·5	Hübl	194	Micko	288·6	Micko	103·8	De Negri and Fabris	25	56·3	Dieterich
90	0·8875	,,			2·3 3·5	De Negri and Fabris					102·6	Micko	40	56·0	,,
					13·4-18[2]	Micko					99·4	Dieterich	50	41·3	,,
											Iodine Value Liquid Fatty Acids.				
											111·1-111·8[3]	Tortelli and Ruggeri			

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[1] Oil from the Punjab. [2] Determined in a capillary tube. [3] Cold pressed oil, eighteen months old. [4] Californian oil. [5] Mogador.

PLUM KERNEL OIL

French—*Huile de prunier.* German—*Pflaumenkernoel.*
Italian—*Olio di prugne.*

For tables of constants see p. 586. The constants given in the tables refer both to expressed and extracted oils.

Plum kernel oil is obtained from the kernels of plums (*Prunus domestica* and *Prunus damascæna*). The oil is light yellow in colour, and possesses an agreeable, mild, almond-like taste.

With nitric acid, of specific gravity 1·4, plum kernel oil assumes an orange colour (like apricot kernel oil). With *Bieber's* reagent, consisting of equal parts (by weight) of concentrated sulphuric acid, fuming nitric acid, and water, a pink colouration is obtained.

The sample examined by *Micko* had the acid value 0·55.

The oil is used chiefly to adulterate almond oil.

[TABLE

Physical and Chemical Constants of Plum Kernel Oil

Specific Gravity		Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.	
At 15° C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.
0·9160	De Negri and Fabris	− 5 to − 6	De Negri and Fabris	191·48	De Negri and Fabris	100·4	De Negri and Fabris	44·5-45	De Negri and Fabris
0·91949	Micko[1]			191·55	Micko	100·2	Micko		
						93·3[3]	Tortelli and Ruggeri		

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.
15-13	De Negri and Fabris	20-22	De Negri and Fabris	200·47	Micko	279·3	Micko	102	De Negri and Fabris
...	...	12·4-18·1[2]	Micko	...	...	...	...	104·2	Micko

Liquid Fatty Acids.	
98·6[3]	Tortelli and Ruggeri

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[1] *Journ. Soc. Chem. Ind.* 1893, 935.

[2] Determined in a capillary tube.

[3] Cold pressed oil, eighteen months old.

PEACH KERNEL OIL

French—*Huile de pêcher.* German—*Pfirsichkernoel.*
Italian—*Olio di pesche.*

For tables of constants see p. 588.

Peach kernel oil (peach oil) is obtained from the kernels of the peach (*Amygdalus persica*). The kernels contain 32-35 per cent of oil.

The oil has a pale yellow colour; it greatly resembles almond oil. *Dieterich* states that the freshly expressed oil—of which he obtained 10-12 per cent from the kernels—smells slightly of hydrocyanic acid. A sample examined by *Lewkowitsch* had the acid value 3·0. With nitric acid of the specific gravity 1·4, peach kernel oil becomes first yellowish brown, afterwards dirty orange. With *Bieber's* reagent it remains unchanged at first,[1] then after about half-an-hour's standing it becomes slightly pink, the pink colour being less strongly developed than is the case with apricot kernel oil. In the phloroglucinol test (see p. 595) peach kernel oil, like apricot kernel oil, gives a red colouration.

This oil is chiefly used for adulteration, or for substitution, of almond oil. The commercial "almond oil French" is frequently a mixture of peach kernel oil with apricot kernel oil (cp. p. 583).

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[1] Lewkowitsch, *Analyst*, 1904, 106.

[TABLE

Physical and Chemical Constants of Peach Kernel Oil.

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.		Refractive Index. Butyro-refractometer.			Refractive Index. Oleo-refractometer.		
At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent	Observer.	°C.	Observer.	At °C.	"Degrees."	Observer.	At °C.	"Degrees," at 22° C.	Observer.
15	0·918	De Negri and Fabris	Below −20	Maben	189·1	Maben	92·5-93·5	De Negri and Fabris	42-43	De Negri and Fabris	25	67·2[1]	Dieterich	22	+7·5 to +11·5	Pearmain
15	0·92147	Micko			192·5	De Negri and Fabris	99·7	Micko			,,	65·7[2]	,,			
15·5	0·9198	Lewkowitsch			191·1	Micko	109·7[1]	Dieterich			,,	66·1	Beckurts and Seiler			
90	0·8899	Dieterich			191·4	Lewkowitsch	98·6[2]	,,			,,	66·5	Mansfeld			
							94·8[3]	Tortelli and Ruggeri			40	58·5[1]	Dieterich			
							110·1	Wijs			,,	57·0[2]	,,			
							95·24	Lewkowitsch			,,	57·5	Lewkowitsch			
											50	52·2[1]	Dieterich			
											,,	51·5[2]	,,			

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.
Titer Test.		3-5	De Negri and Fabris	200·9	Micko	278·8	Micko	94·1	De Negri and Fabris
13-13·5	Lewkowitsch	10-18·9	Micko	205·0	Lewkowitsch	...	...	101·9	Micko
				...	...			Liquid Fatty Acids.	
								101·9[3]	Tortelli and Ruggeri

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[1] Freshly prepared oil. [2] Old oil. [3] Cold pressed oil, eighteen months old.

ALMOND OIL

French—*Huile d'amande.* German—*Mandeloel.*
Italian—*Olio di mandorle.*

For tables of constants see pp. 590-592.

Almond oil is expressed [or extracted] chiefly from bitter almonds, the seeds of *Prunus amygdalus*, var. *amara*. Bitter almonds yield more oil than sweet almonds. The latter (from *Prunus amygdalus*, var. *dulcis*) are but rarely used alone for the preparation of almond oil. Mogador bitter almonds are always more or less mixed with sweet almonds.

The oils obtained from both varieties are practically identical, so that no definite difference can be established by chemical means; this will be seen by a glance at the accompanying table. The principal countries from which almonds are supplied are Morocco, Canary Islands, Portugal, Spain, France, Italy, Sicily, Syria, and Persia.

The almonds contain from 38 to 45 per cent of oil.

Almond oil is, according to *Gusserow*, free from stearin; this is confirmed by *Hehner* and *Mitchell*.[1] The glycerides in almond oil consist chiefly of olein; the high iodine value points, however, to the presence of glycerides of fatty acids belonging to a less saturated series than the oleic. Indeed, *Farnsteiner* has isolated from the mixed fatty acids linolic tetrabromide in a quantity corresponding to 5·79 per cent of linolic acid.

Contrary to older statements, almond oil does not turn easily rancid. A number of genuine almond oils, 12 to 18 months old, examined in my laboratory, had acid values varying from 0·79 to 3·1 (see table, p. 595).

Almond oil is largely used in pharmaceutical practice, hence the pharmacopœias of the different countries prescribe certain reactions for identification. Most of these, such as the specific gravity test and the elaïdin test, are of very little use for purposes of identification. Of greater importance is the determination of the melting point of the mixed fatty acids, almond oil being characterised by the low melting point of its mixed fatty acids. According to the German Pharmacopœia the mixed fatty acids of pure almond oil should remain liquid at 15° C. for an indefinite length of time; mixed with an equal volume of alcohol they should give a clear solution at 15° C., and not become turbid on adding twice the volume of alcohol. *Olive*, *sesamé*, *arachis*, and *cotton seed oils* may thus be recognised. *Apricot* or *peach kernel oils* will, however, escape detection.

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[1] *Analyst*, 1896, 328.

Physical and Chemical Constants of Almond Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.	
At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
12	0·9168[1]	Mills and Akitt	–10	Girard	195·4	Valenta	98·4	Hübl
,,	0·9154[2]	,,	–21	Maben	190·9	Dieterich	96·6-99·2	Beringer
15	0·917-0·920	Chateau			190·5-191·2[2]	De Negri and Fabris	96·2-101·9	Dieterich
,,	0·914-0·920	Allen						
,,	0·9180	Maben			189·5-191·7[1]	,,	97·5	Del Torre
,,	0·9186	Valenta					98-99	Peters
,,	0·9183	Massie					98·4[2]	Moore
,,	0·9190	Del Torre					93-95·4[2]	De Negri and Fabris
,,	0·9190-0·9195[2]	De Negri and Fabris					94·1-96·5[1]	,,
,,	0·9175-0·9195[1]	,,					95·8[2]	Tortelli and Ruggeri
,,	0·9177-0·9185	Allen and Brewis					95·8-101·26	Allen and Brewis
15·5	0·9186	Tolman and Munson					98·5-100·2[2]	Lewkowitsch
,,	0·9178-0·9183	Lewkowitsch						

[1] From bitter almonds.

[2] From sweet almonds.

Physical and Chemical Constants of Almond Oil—continued

Hehner Value.		Thermal Tests.				Refractive Index.		
		Maumené Test.		Heat of Bromination.				
Per cent.	Observer.	°C.	Observer.	°C.	Observer.	At °C.		Observer.
96·2	West-Knight	52-54	Maumené	17·6	Hehner and Mitchell	15·5	1·4728	Tolman and Munson
		53	Del Torre					
		51-52 [2]	De Negri and Fabris [3]	20·25	Bromwell and J. L. Meyer	60	1·4555	Thoerner
		51-53 [1]	,,	20·6-21	Allen and Brewis			
						Oleo-refractometer.		
						"Degrees."		Observer.
						+ 6		Jean
						+ 7		Bruyn and van Leent
						+8 to + 10·5 at 22° C.		Pearmain
						Butyro-refractometer.		
						At °C.		Observer.
						15·5	70·9	Tolman and Munson
						25	64·8	Beckurts and Seiler
						,,	64·0	Dieterich

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[1] From bitter almonds.

[2] From sweet almonds.

[3] Jeans' thermelaeometer.

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.		Refractive Index.	
°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	At 60° C.	Observer.
Titer Test.		14	Hübl	204	Thoerner	93·5-95·5 [2]	De Negri and Fabris	1·4461	Thoerner
9·5-10·1 [2]	Lewkowitsch	13-14 [1 & 2]	De Negri and Fabris			94·1-96·5 [1]	,,		
11·3-11·8 [1]	,,								
						Liquid Fatty Acids.			
						101·7 [2]	Tortelli and Ruggeri		

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[1] From bitter almonds.

[2] From sweet almonds.

Older statements that almond oil is adulterated with the following oils:—poppy seed, walnut, cotton seed, sesamé, arachis, olive, lard oils, hardly hold good in the case of the almond oils found in commerce to-day. It need, therefore, only be briefly pointed out that poppy seed, walnut, cotton seed, and also sesamé oils would be detected by a higher iodine value than the normal one. The confirmatory tests to be applied would be:—in the case of cotton seed oil, the *Halphen* colour test, and especially the melting point of the mixed fatty acids; and in the case of sesamé oil, the *Baudouin* colour reaction. Arachis oil would be identified by the isolation of arachidic acid; olive oil by the high melting point of the fatty acids, and the solidifying point of the oil itself; lard oil by the phytosteryl acetate test.

The chief adulterants of almond oil are apricot kernel oil and peach kernel oil. The last two oils are used to such an extent, that they frequently completely substitute almond oil; indeed "foreign" almond oil, or "oil of sweet almonds, French," *Oleum Amygdalarum Gallicum*, is nothing else but apricot kernel oil and peach kernel oil. Genuine almond oil is sold commercially under the name "almond oil, English." Pure almond oil may be differentiated from apricot and peach kernel oils by its lower iodine value, so that an almond oil having an iodine value exceeding 105 must be looked upon with suspicion. The differentiation of almond oil from the two oils by means of the colour tests described below will not lead to decisive results in each case, owing to the different behaviour of almond oil from various sources.

The close relationship in which apricot kernel and peach kernel oils stand to almond oil renders detection of these oils in an almond oil a very difficult problem, which cannot be solved with certainty in the present state of our knowledge, since most of the physical and chemical characteristics, including the iodine value, fail to reveal the presence of the kernel oils.

In doubtful cases, recourse may be had to the following colour reactions, which should, however, be looked upon as confirmatory tests only, and as more suitable for differentiating peach kernel and apricot kernel oils severally from almond oils, than to detect the former oils when they are admixed with almond oil.

The Nitric Acid Test.—Almond oil, on being shaken with nitric acid of specific gravity 1·4, remains colourless, or becomes only slightly yellow, whereas apricot kernel oil assumes an orange yellow, and peach kernel oil becomes yellowish brown, subsequently passing into a dirty orange colour.

Bieber's Test is carried out by agitating five volumes of oil with one volume of a mixture consisting of equal parts (by weight) of concentrated sulphuric acid, fuming nitric acid, and water. Pure almond oil does not change its colour, whereas apricot kernel oil gives a pink (peach-blossom) colour, and peach kernel a faint pink colouration after standing for some little time. I find that it is necessary to prepare *Bieber's* reagent afresh for each set of tests; it should also be noted that the colour reaction is much more distinct in the case of freshly expressed oil than in the case of a sample which has been kept for half a year and longer (*Lewkowitsch*).

Whereas it is thus possible to broadly differentiate almond oil from apricot and peach kernel oils, it would be hazardous to pronounce adulteration on the strength of these colour tests alone. Mixtures of almond oil and apricot kernel oil containing one-half of the latter still show distinctly the colour reaction of the latter, but mixtures containing 25 per cent of apricot kernel oil can no longer be detected with certainty (*Lewkowitsch*[1]).

Recently, $\frac{1}{10}$th per cent solution of phloroglucinol in ether, applied in the presence of nitric acid, has been proposed as a test for apricot kernel and peach kernel oils.[2] Nitric acid of specific gravity 1·45 gives in my experience better results than acid of 1·42 specific gravity, recommended by *Chwolles.* Undoubtedly apricot kernel oil and peach kernel oil give distinct deep red colourations with the reagent, in contradistinction to some almond oils; yet other specimens of genuine almond oils tested by me (see table, p. 595) show more or less strongly the same reaction. This test must, therefore, be employed with even greater circumspection than the *Bieber* test.

In the following table I have collated a number of tests carried out with genuine almond oils. On comparing the numbers with those given for apricot and peach kernel oils, they will, in doubtful cases, render some assistance to the analyst.

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[1] *Analyst*, 1904, 106.

[2] Chwolles, *Pharm. Zeit.* 1903, 109. The reagent was first proposed by Kreiss.

[TABLE

Characteristics of some Almond and Allied Oils (Lewkowitsch)

Description of Oil.	Specific Gravity.	Saponification Value.	Iodine Value.	Butyro-refractometer at 40° C.	Acid Value.	Fatty Acids.		Colour Reactions.	
						Neutralisation Value.	Saponification Value.	Bieber's Test.	Phloroglucinol Test.
Almond Oils, expressed from—				" Degrees."					
1. Valencia Sweets . . .	0·91995	207·6	99·4	57·5	5·16	207·8	207·6	Colourless	No colouration
2. Blanched Valencia Sweets .	0·9182	191·7	103·6	57·5	2·9	196·4	201·7	,,	No crimson colouration
3. Sicily Sweets . . .	0·9178	183·3	100·3	57·0	0·79	198·8	202·2	,,	,, ,,
4. Mazagan Bitters . . .	0·9180	188·6	102·5	56·5	3·1	196·8	203·1	,,	Slightly crimson
5. Small Indian Almonds .	0·91907	189·2	96·65	57·0	2·9	195·8	200·7	,,	,, ,,
6. Mogador Bitters . . .	0·9183	194·98	104·2	57·0	1·3	197·1	203·2	,,	No crimson colouration
7. Peach Kernel Oil	0·9198	191·4	95·24	57·5	3·0	196·8	205·0	Colourless at first, then pink	Deep crimson ,,
8. Apricot ,, ,, ...	0·9200	192·4	107·4	58·0	2·3	198·0	202·0	Pink colouration	,, ,, ,,
9. ,, ,, ,, from Mogador Kernels	0·9172	198·2	107·9	57·0	2·8	194·0	200·7	Slightly pink	Less deep crimson than 8
10. Californian Apricot Kernel Oil .	0·92026	190·3	108·7	58·0	1·2	197·8	202·8	Very slightly pink	,, ,, ,,

The following numbers, representing the refractive indices of the ten oils for different rays, have been determined by *Ross*;[1] unfortunately, the numbers given below do not furnish an analytical means of differentiating almond oil from the related oils.

Refractive Indices at 20 Degrees Centigrade (Ross)

Oil	D	C	F	G
No. 1	1·4715	1·4688	1·4780	1·4835
,, 2	1·4715	1·4688	1·4780	1·4836
,, 3	1·4711	1·4685	1·4777	1·4833
,, 4	1·4712	1·4686	1·4778	1·4834
,, 5	1·4710	1·4685	1·4777	1·4833
,, 6	1·4714	1·4688	1·4780	1·4835
,, 7	1·4710	1·4685	1·4776	1·4832
,, 8	1·4717	1·4692	1·4784	1·4839
,, 9	1·4715	1·4690	1·4782	1·4837
,, 10	1·4725	1·4700	1·4792	1·4847

WHEAT-MEAL OIL

French—*Huile de farine de froment.* German—*Weizenmehlöl.*
Italian—*Olio di farina di frumento.*

This oil was extracted from wheat flour.[2] It must not be confounded with wheat oil.

Physical and Chemical Constants of Wheat-Meal Oil

Specific Gravity at 100° (water 15° C.=1).	Saponification Value.	Reichert-Meissl Value.	Iodine Value.	Refractive Index. At 25° C.
0·9068	166·5	2·8	101·5	1·4851
				Butyro-refractometer.
				92

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[1] *Analyst*, 1904, 106.
[2] Spaeth, *Analyst*, 1896, 234.

SANGUINELLA OIL[1]—DOGWOOD OIL

French—*Huile de cornouiller.* German—*Hartriegeloel.*
Italian—*Olio di Sanguinella.*

Physical and Chemical Constants of Sanguinella Oil

Specific Gravity at 15° C.	Solidifying Point. °C.	Saponific. Value. Mgrms. KOH.	Iodine Value. Per cent.	Maumené Test. °C.
0·921	– 15	192·05	100·8	52

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point. °C.	Melting Point. °C.	Neutralisation Value. Mgrms. KOH.	Iodine Value. Per cent.
31-29	34-37	195·1	102·75

This oil is obtained from the seeds of the dogwood (cornel tree), *Cornus sanguinea.* It has a green-yellowish colour; its odour is similar to that of low-grade olive oil. The oil is used as a burning oil, and for soapmaking.

ACORN OIL[2]

French—*Huile de gland.* German—*Eicheckernoel.*
Italian—*Olio di ghiande.*

This oil is obtained by extracting the fruit of *Quercus agrifolia*; it is a deep brown fluorescent oil. On long standing it deposits "stearine."

Physical and Chemical Constants of Acorn Oil

Specific Gravity at 15° C.	Solidifying Point. °C.	Saponification Value.	Iodine Value.	Maumené Test. °C.	Refractive Index.
0·9162	10	199·3	100·7	60[3]	1·4731

The melting point of the fatty acids is 25° C.

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[1] De Negri and Fabris, *Annali*, etc., 181.

[2] Blasdale, *Journ. Soc. Chem. Ind.* 1896, 206.

[3] Jean's thermelaeometer.

CALIFORNIAN NUTMEG OIL[1]

French—*Huile de Noix de Californie.* German—*Kalifornisches Muskatoel.* Italian—*Olio di Noci di California.*

California nutmeg oil is obtained from the fruit of *Tumion Californicum.*

Physical and Chemical Constants of Californian Nutmeg Oil

Specific Gravity at 15° C.	Saponific. Value. Mgrms. KOH.	Iodine Value. Per cent.	Maumené Test. °C.	Refractive Index.
0·9072	191·3	94·7	77[2]	1·4766

The melting point of the fatty acids is 19° C.

* ARACHIS OIL, PEANUT OIL, EARTHNUT OIL

French—*Huile d'arachide.* German—*Arachisoel, Erdnussoel.* Italian—*Olio di arachide.*

For table of constants see pp. 600-602.

Arachis oil is obtained from the earthnuts, the seeds of *Arachis hypogæa* (Leguminosæ), a plant largely cultivated on the West Coast of Africa, in India, North America (chiefly Virginia, Georgia, Tennessee, and North Carolina), South of Europe, etc.

The nuts are first shelled by special machinery, and the inner or red skin which surrounds the kernel is removed as completely as possible by a blast of air, in a manner similar to that employed for cleaning wheat in flour mills. The separated and cleaned kernels are then ground and subjected to hydraulic pressure. Since the kernels contain from 43-45 per cent of oil, expression of the oil is carried out in two stages, as described in chap. xiii.

It should be noted that arachis oil is usually pressed in the same establishment where sesamé oil is pressed, and as it is impossible to keep presses and press cloths separate for each kind of oil, commercial arachis oil contains a sufficient amount of sesamé oil to give faintly the colour reaction of sesamé oil. Due regard should be had to this fact in judging a commercial sample of arachis oil which gives a faint *Baudouin* reaction.[3]

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[1] Blasdale, *Journ. Soc. Chem. Ind.* 1896, 206.

[2] By Jean's thermelacometer.

[3] Cpr. also Fendler, *Zeit. f. Untcrs. Nahrungs. u. Genussm.* 1903, 411.

* [illegible]

The "cold-drawn oil" of the first expression is nearly colourless, and has a pleasant taste resembling the flavour of kidney beans. It is used as salad oil. The oil obtained by second expression also serves as an edible oil or for burning. The third quality expressed at a higher temperature is chiefly used for soap-making. This oil is somewhat thick and turbid, and must therefore be filtered to render it bright. A comparison of specific gravities and iodine values of different arachis oils of first expression and second expression has been given by *Wijs.*[1] For edible purposes the oil is required to be almost water white and is hence filtered over fuller's earth or charcoal (cp. chap. xv., edible oils).

On standing at a little above 0° arachis oil deposits "stearine." Owing to the arachin which this "stearine" contains, it does not readily settle out as a crystalline mass. A number of experiments I have carried out[2] show that even when crystals are obtained once, the very slight rise of temperature caused by handling the material suffices to either melt the crystalline mass, or to convert it into a gelatinous form, which withstands all attempts at filtering.

On allowing the separated "stearine" to settle out by prolonged standing in the cold, an arachis oil less rich in solid glycerides can be drawn off from the separated stearine. A "margarine d'arachide" of the iodine value 79·4, melting point 21·5° C., most likely represents the "stearine" so obtained on a large scale.[1]

Palmitic acid, stated by *Caldwell*[3] to occur in arachis oil, could not be detected by *Kreiling*[4] without, however, absolute proof of its absence having been adduced. The latter chemist has shown that besides arachidic acid (melting point 74·5° C.), as proved by *Gössmann's* researches, another solid fatty acid, of the melting point 81° C., viz. lignoceric acid, occurs in combination with glycerol. Lignoceric acid, being less readily soluble in alcohol than arachidic acid, may be separated from the latter by means of this solvent (cp. below). The presence of stearic acid amongst the solid fatty acids appears to be certain, a specimen examined by *Hehner* and *Mitchell*[5] having given 7 per cent of stearic acid crystals of the melting point 67° C. It is very likely that the "stearic" acid was contaminated with "arachidic" acid, of which arachis oil contains about 5 per cent.

Amongst the liquid fatty acids of arachis oil *Gössmann* and *Scheven*,[6] and also *Schröder*,[7] claim to have found the unsaturated fatty acid—hypogæic acid (p. 101). *Schoen*,[8] however, having been unable to detect this acid, asserts that oleic acid is the only unsaturated acid in arachis oil. *Hazura's*[9] conjecture that hypogæic acid forms a constituent of the unsaturated glycerides in arachis oil is confirmed by the fact that synthetical hypogæic acid has the same properties as the natural acid found in arachis oil by *Gossmann* and *Scheven*, and *Schröder* (cp. chap. iii. 101).

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[1] Wijs, *Zeit. f. Unters. Nahrungs. u. Genussm.* 1903, 492.

[2] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1903, 592.

[3] *Liebig's Annalen*, 101. 97.

[4] *Berichte*, 21. 880.

[5] *Analyst*, 1896, 328.

[6] *Liebig's Annalen*, 94. 230.

[7] *Ibid.* 143. 22.

[8] *Ibid.* 244. 253 ; *Berichte*, 21. 878.

[9] *Monatshefte*, 10. 242.

Physical and Chemical Constants of Arachis Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.	
At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.
15	0·9193	Valenta	− 2·5	Schoen	190·1-197	Dieterich	103	Hübl	0·0	Crossley and Le Sueur
,,	0·9173	Del Torre	0 to +2	Lewkowitsch	189·3[1]	Thomson and Ballantyne	87·3-90	Dieterich	0·48[10]	Sadtler
,,	0·9171[1]	Thomson and Ballantyne	+3[10]	Sadtler	191·1[2]	,,	96·7-98·7	Filsinger	1·60[11]	,,
,,	0·9209[2]	,,	+3[11]	,,	192·7-194·6	Schoen	101·3	Del Torre		
,,	0·917[2]	De Negri and Fabris	+2[12]	,,	190·2[2]	De Negri and Fabris	85·6-98·4	Schoen		
,,	0·9200[3 4]	,,			193·1[3]	,,	95-95·4[3]	De Negri and Fabris		
,,	0·9165[5]	,,			191·4-192[4]	,,	97·9-100[4]	,,		
,,	0·917[10]	Sadtler			189·4[5]	,,	92-92·7[5]	,,		
,,	0·9175[11]	,,			185·6-194·8[8]	Crossley and Le Sueur	90·2	Lewkowitsch		
,,	0·911[12]	,,			191-196	Oliveri	101-105	Oliveri		
15·5 (water 15·5=1)	0·9195	Crossley and Le Sueur			194-196	Thoerner	96·55-98·98	Schweitzer and Lungwitz		
	0·9256[8]	,,					94-96	Thoerner		
15·5	0·9186-0·9188	Tolman and Munson					92·4-100·82[8]	Crossley and Le Sueur		
,,	0·91795	Lewkowitsch					83·3-84·1[6]	Tortelli and Ruggeri		
20	0·9118-0·9125[12]	Wijs					84·6[8]	,,		
,,	0·9139-0·9145[10]	,,					91·75[10]	Sadtler		
,,	0·9153[13]	,,					94·17[11]	,,		
22	0·911-0·916	Schoen								
23	0·917-0·918	Dieterich								
99 (water 15·5=1)	0·8673	Allen								

[1] Refined oil.
[2] Commercial oil.
[3] From Pondichéry nuts.
[4] From Coromandel nuts.
[5] From Mozambique nuts.
[6] From Rufisque nuts.
[7] From Boulam nuts.
[8] East Indian oils; the acid values of these oils, four in number, are recorded in the table p. 603.
[9] Jean's thermelaeometer.
[10] Virginian nuts, *Amer. Journ. Phar.* 1897, 69, 490-492.
[11] Spanish nuts, *Amer. Journ. Pharm.* 1897, 69, 490-492.
[12] African nuts, *Amer. Journ. Pharm.* 1897, 69, 490-492.
[13] Egyptian nuts.

Physical and Chemical Constants of Arachis Oil—continued

Hehner Value.	
Per cent.	Observer.
95·86	Bensemann
94·87[10]	Sadtler
95·31[11]	,,

Maumené Test.	
°C.	Observer.
56-75[10]	Sadtler
58	Del Torre
49[3]	De Negri and Fabris[9]
51[4]	,,
46[5]	,,
45·5[2]	,,
49	Archbutt

Specific Temperature Reaction.	
105[1]	Thomson and Ballantyne
137[2]	,,

Refractive Index.		
At °C.		Observer.
15	1·4731	Procter
15·5	1·4723	Tolman and Munson
60	1·4545	Thoerner

Oleo-refractometer.	
" Degrees " at 22° C.	Observer.
+3·5[6] to +6·5[7]	Jean
+4	Bruyn and van Leent
+5 to +7	Pearmain

Butyro-refractometer.		
At °C.		Observer.
15·5	70-71·3	Tolman and Munson
25	66·5	Beckurts and Seiler
,,	65·8-67·5	Mansfeld
40	57·5	Crossley and Le Sueur

Viscosity.	
No. of Seconds At 70° F.	Observer.
350·1[8]	Crossley and Le Sueur
347·0	,,
429·3	,,
306·9	,,

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[1] Refined oil. [2] Commercial oil. [3] From Pondichéry nuts. [4] From Coromandel nuts. [5] From Mozambique nuts. [6] From Rufisque nuts. [7] From Boulam nuts. [8] East Indian oils; the acid values of these oils, four in number, are recorded in the table p. 603. [9] Jean's thermelaeometer. [10] Virginian nuts, *Amer. Journ. Pharm.* 1897, 69, 490-492. [11] Spanish nuts, *Amer. Journ. Pharm.* 1897, 69, 490-492. [12] African nuts, *Amer. Journ. Pharm.* 1897, 69, 490-492. [13] Egyptian nuts.

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.			Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.		Refractive Index	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.	At 60° C.	Observer.
92·5	0·8436	Schoen	23·8	Hübl	27·7	Hubl	201·6	Thoerner	281·8	Allen	95·5-96·9	Morawski and Demski	1·4461	Thoerner
98·5	0·8468	,,	28	Allen	27·8-29·5	Allen								
99 (water 15·5=1)	0·846	Allen	29-29·5	Dieterich	31·5-32	Dieterich					103·42 [2]	De Negri and Fabris		
					31-32 to 34-35	Bensemann [5]					96·53 [4]	,,		
100 (water 100=1)	0·8790	Archbutt	31	Bach	33	Bach					96-97	Thoerner		
					30	Schoen								
					29-31 [1]	De Negri and Fabris								
			25-23 [1]	De Negri and Fabris	28-30 [2]	,,					Iodine Value of the Liquid Fatty Acids.			
			25-22 [2]	,,	27-29 [3]	,,								
			24-22 [3]	,,	28-30 [4]	,,								
			25-23 [4]	,,	30-32	Thoerner					128·5	Wallenstein and Finck		
			29-30	Thoerner	34 [9]	Sadtler					111·0-119·5	Lane		
			32·5 [9]	Sadtler	29 [10]	,,					122·4-123·4 [6]	Tortelli and Ruggeri		
			27·5 [10]	,,							104·7-105·5 [7]	,,		
			Titer Test.								106 [8]	,,		
			28·1-29·2 [4]	Lewkowitsch										

[1] From Pondichéry nuts.
[2] From Coromandel nuts.
[3] From Mozambique nuts.
[4] Commercial oil.
[5] Bensemann's method.
[6] Iodine value of oils : 92·2-93·5.
[7] From Rufisque nuts ; iodine value of oil : 83·3-84·1.
[8] From Gambia nuts ; iodine value of oil : 84·6.
[9] Spanish nuts.
[10] Virginian nuts.

Amongst the liquid fatty acids of arachis oil *Hazura* and *Grüssner* identified linolic acid by its oxidation product sativic acid. The amount of linolic acid from an arachis oil, having the iodine value 82·9, was calculated by *Farnsteiner* from the isolated tetrabromide as about 6 per cent of the mixed fatty acids. Judging from the iodine value of the liquid fatty acids, as given in the table of constants of the mixed fatty acids, this proportion appears much too low. In somewhat better agreement with the numbers given in the table is the statement, also due to *Farnsteiner*, that the mixed fatty acids contain, besides oleic acid, 30·3 per cent of liquid fatty acids, of which linolic acid only forms a fraction. Since arachis oil contains no linolenic acid, the deficiency of unsaturated acids (to account for the high iodine value of the mixed liquid fatty acids) may perhaps be explained, pending further investigation, by the assumption that hypogaeic tetrabromide is soluble in petroleum ether.

The true acetyl value of a sample of arachis oil examined in my laboratory—having the acid value 2·17—was 9·02 to 9·09. The "cold-drawn" oils contain small amounts of free fatty acids only; their amount is somewhat higher in the commercial oils intended for technical purposes. In the following table I collate a number of observations:—

No.	Description of Oil.	Number of Samples.	Free Fatty Acids in terms of Oleic Acid.	Observer.
			Per cent.	
1	Expressed, salad oil .	13	0·85 to 3·91	Nördlinger
2	Expressed, commercial oil	12	3·58 to 10·61	,,
3	Extracted oil . . .	16	0·95 to 8·85	,,
4	Refined oil . . .	1	0·62	Thomson and Ballantyne
5	Commercial oil . .	1	6·20	,,
6	Indian oil . . .	1	2·9	Crossley and Le Sueur
7	,, ,, . . .	1	4·8	,,
8	,, ,, . . .	1	16·5	,,
9	,, ,, . . .	1	13·1	,,

Oils No. 4 and No. 5 of the table contained 0·54 and 0·94 per cent of unsaponifiable matter respectively.

Samples No. 6, 7, 8, 9, examined in a Laurent polarimeter, showed in a 200 mm. tube the rotations $-0°7'$, $+0°24'$, $\pm 0°0'$, and $-0°7'$ respectively; the optical activity cannot, therefore, be caused by the glycerides themselves.

Arachis oil can be identified and detected with certainty by the isolation of "arachidic acid." The arachidic acid obtained by the following method is in truth a mixture of arachidic and lignoceric acids, and will be termed here "crude arachidic acid."

The method originally proposed by *Renard*[1] is carried out in the following manner:—Saponify 10 grms. of the oil, separate the fatty

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[1] *Compt. rend.* 73. 1330.

acids from the soap solution by hydrochloric acid, dissolve these in 90 per cent alcohol, and add a solution of lead acetate. I shorten the process by neutralising the excess of alkali with acetic acid, using phenolphthalein as an indicator, and precipitating with lead acetate without isolating the fatty acids.[1] Filter off the precipitated lead salts, and extract them with ether in a Soxhlet apparatus, thus separating the lead salts of the unsaturated acids from the lead salts of the saturated fatty acids. Decompose the latter with hydrochloric acid under ether, separate the ethereal layer of the fatty acids from the lead chloride which remains partly in solution and distil off the ether. Next dissolve the residue in 50 c.c. of hot 90 per cent alcohol. If arachis oil is present in the sample, a crop of crystals consisting of crude arachidic acid will be obtained on cooling the alcoholic solution. Filter the crystals off and wash on the filter, first with a measured quantity of 90 per cent, then with 70 per cent alcohol, which dissolves but small quantities thereof, and finally dissolve them by pouring boiling absolute alcohol on the filter, receiving the filtrate in a porcelain dish or in a flask. Evaporate to dryness and weigh the residue. Add to the weight of crude arachidic acid thus found the quantity dissolved by the 90 per cent alcohol used for washing, taking as basis for calculation that 100 c.c. dissolve 0·022 grm. at 15° C., or 0·045 grm. at 20° C. Finally determine the melting point of the crude arachidic acid, which should be from 71° to 72° C. *Renard* has isolated 4·5 to 5·0 per cent, *Allen* 5·5, and *De Negri* and *Fabris* 4·37 to 4·80 per cent of "arachidic acid" from samples of genuine arachis oil. Hence the amount of acid found will represent roughly a $\frac{1}{20}$ of the arachis oil present, and the latter may therefore be approximately calculated by multiplying the weight of the crude arachidic acid by 20. *Bellier*[2] proposes the factor 23·81.

To test the accuracy of the method *De Negri* and *Fabris*[3] have examined prepared mixtures of olive oil and arachis oil and obtained the following numbers:—

Sample Containing		Crude Arachidic Acid Found.			Arachis Oil Found.
Olive Oil.	Arachis Oil.	Weighed as Crystals.	Calculated as Dissolved.	Total.	Per cent.
Per cent.	Per cent.	Grms.	Grms.	Grms.	
70	30	0·107	0·0315	0·1385	29·08
80	20	0·0605	0·0315	0·0920	20·24
85	15	0·0385	0·0315	0·070	14·00
90	10	0·0200	0·0315	0·0515	10·30
90	10	traces			
90	10	0·0280	0·0154	0·0434	9·54
90	10	traces			

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[1] Kreis (*Journ. Soc. Chem. Ind.* 1895, 688) employs an *alcoholic* solution of lead acetate.

[2] *Ann. chim. anal. appl.* 1899 [4], 4.

[3] *Annali del Laboratorio Chimico delle Gabelle*, 1891-92, 123.

It will thus be seen that on employing 10 grms. of the sample, the limit is reached if it contain only 10 per cent of arachis oil. It will therefore be advisable to take from 20 to 40 grms. of the sample according to the quantity of arachis oil it may be suspected to contain, and to double or quadruple the proportions of 90 per cent alcohol required to dissolve the solid fatty acids.

Tortelli and *Ruggeri*,[1] in an exhaustive examination of *Renard's* method, found that the solubilities in 90 per cent alcohol, as given by *Renard*, are too low. Their method of isolating the crude arachidic acid (see below) leads to a mixture of acids melting between 74° C. and 75·5° C., for which the following solubilities have been ascertained :—

100 *c.c. of* 90 *per cent Alcohol dissolve Crude Acid of M.P.* 74°-75·5° *C.*

Amount of Acid taken.	Of Melting Point.	Amount of Acid dissolved			The amount of Crude Acid employed corresponds to
		At 15° C.	17·5° C.	20° C.	
Grms.	°C.	Grms.	Grms.	Grms.	
2·7000	74·3-74·5	0·0729	0·0820	0·0910	More than 20 grms. of arachis oil
1·5600	75·1-75·5	0·0715	0·0801	0·0922	
1·2506	74·8-75·5	0·0730	0·0811	0·0902	
1·0000	74·3-74·5	0·0688	0·0866	0·0914	About 20 grms. of arachis oil
0·9604	74·0-74·6	0·0680	0·0869	0·0918	
0·5503	74·0-74·6	0·0650	0·0806	0·0879	Mixtures containing about 50 per cent of arachis oil
0·5008	74·0-74·6	0·0643	0·0799	0·0844	
0·3899	74·4-75·5	0·0602	0·0673	0·0740	Mixtures containing 40 per cent of arachis oil
0·2615	74-75	0·0539	0·0610	0·0680	Mixtures containing 27 per cent of arachis oil
0·1690	74-75	0·0447	0·0544	0·0662	Mixtures containing 18 per cent of arachis oil
0·1064	74-75	0·0343	0·0402	0·0472	Mixtures containing 11 per cent of arachis oil
0·0504	74·7-75·5	0·0301	0·0398	...	Mixtures containing 5 per cent of arachis oil
0·0505	74·2-74·6	0·0314	0·0410	...	

For practical purposes these numbers may be condensed as follows :—

100 *c.c. of* 90 *per cent Alcohol dissolve Crude Acid of M.P.* 74°-75·5° *C.*

For Amount of Acid	At 15° C.	17·5° C.	20° C.
From 2·7 down to 0·5 grms.	0·070	0·080	0·090
,, 0·47 ,, 0·17 ,,	0·050	0·060	0·070
,, 0·11 ,, 0·05 ,,	0·033	0·040	0·045

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[1] *Journ. Soc. Chem. Ind.* 1898, 877.

In order to obtain crude arachidic acid of a melting point 74°-75·5° C. *Tortelli* and *Ruggeri* modify the *Renard* test in the following manner :—The lead salts of the solid fatty acids are prepared from 20 grms. of oil as described above, and the liberated solid acids are dissolved in 100 c.c. of 90 per cent alcohol by warming on the water-bath to about 60° C. If a slight turbidity be noticeable one drop of very dilute hydrochloric acid may be added. Then allow to stand for three hours at a temperature of 15° to 20° C. The acid which separates out on cooling is brought on a filter, the filtered alcoholic solution being used to transfer the crystals completely on to the filter ; finally they are washed three times each with 10 c.c. of 90 per cent alcohol, and then several times with 70 per cent alcohol. The crystals on the filter are next dissolved in boiling absolute alcohol, the solution being received in a flask. The absolute alcohol is distilled off, the residue dissolved in 100 c.c. of 90 per cent alcohol as described already, and the crystals washed on a filter with 90 per cent and 70 per cent alcohol exactly as before. The washing with 70 per cent alcohol is discontinued when the wash-alcohol no longer dissolves appreciable quantities. Finally the crystals are dissolved in absolute alcohol, and their weight is determined.

The crystals should then melt between 74° and 75·5° C. On observing the alcoholic solution of the solid fatty acids when taken from the water-bath to cool, it will be readily noticed that the crystals represent a mixture of arachidic and lignoceric acids. At first very fine, lustrous needles separate in tufts—lignoceric acid ; afterwards there appear larger quantities of very thin, shining laminæ of nacreous lustre—arachidic acid. The separation commences in the case of pure arachis oil at about 35° to 38° C., the temperature of crystallisation falling as the proportion of arachis oil in a given oil decreases (cp. table, p. 607). The following table gives the amounts of "arachidic acid" found in some arachis oils by *Tortelli* and *Ruggeri* :—

Crude Arachidic Acid found in Arachis Oils

Source of Oil.	Crude Acid.	
	Per cent.	Melting Point. °C.
Buenos Ayres, expressed at 45 to 50° C.	5·24	74·4-74·7
,, extracted with ether	4·92	74·2-74·8
Rufisque, first expression	4·31	74·2-74·6
,, second expression	4·55	74·4-75·2
Gambia, first expression	4·59	74·5-75·1
Commercial, French	5·33	74·1-74·4
,, Spanish	5·40	74·3-75·4

For practical purposes, when the amount of arachis oil in admixture with other oils has to be determined, it will be near enough to take 4·8 per cent as the mean proportion of crude arachidic acid, melting point 74°-75·5° C. in commercial arachis oils.

The following table may serve as a corollary to the one given by *De Negri* and *Fabris*; the numbers are due to *Tortelli* and *Ruggeri*:—

Sample containing		Temperature at which crystals separate from 90 per cent Alcohol.		Crude Arachidic Acid Found.				M.P. of Crystals.	Arachis Oil found.
Olive Oil.	Arachis Oil.		90 per cent Alcohol used.	Weighed as Crystals.	Dissolved (calculated).	Total.			
Per cent.	Per cent.	°C.	c.c.	Grms.	Grms.	Grms.	Per cent.	°C.	Per cent (approx.)
0	100	37·7	260 at 15° C.	0·8894	0·1768	1·0662	5·33	74·1-74·3	100
40	60	31·8	150 ,, 17·5	0·5231	0·1200	0·6431	3·22	74-74·6	60
50	50	29·0	250 ,, 75	0·3931	0·1500	0·5431	2·72	74-74·6	50
60	40	25·5	280 ,, 75	0·2770	0·1509	0·4279	2·14	74·5-75·1	40
70	30	23·2	260 ,, 75	0·2056	0·1300	0·3356	1·68	74·1-74·6	31
80	20	21·0	250 ,, 75	0·1260	0·1150	0·2410	1·21	73·9-74·4	22
90	10	18·8	220 ,, 15	0·0514	0·0682	0·1196	0·60	72·2-74·6	11
95	5	16·7	150 ,, 15	0·0241	0·0434	0·0675	0·34	73-73·5	6·7

Archbutt[1] confirms the numbers given by *Tortelli* and *Ruggeri* for the solubilities of crude arachidic acid, and computes the following corrections:—

Correction per 100 *c.c. of* 90 *per cent Alcohol used for Crystallisation and Washing*

For Weights of Fatty Acids obtained by Renard's Process.	Grms. at		
	15° C.	17·5° C.	20° C.
0·1 or less . .	+0·033	+0·039	+0·046
0·2 ,, . .	0·048	0·056	0·064
0·3 ,, . .	0·055	0·064	0·074
0·4 ,, . .	0·061	0·070	0·080
0·5 ,, . .	0·064	0·075	0·085
0·6 ,, . .	0·067	0·077	0·088
0·7 ,, . .	0·069	0·079	0·090
0·8 ,, . .	0·070	0·080	0·091
0·9 and upwards .	0·071	0·081	0·091

Archbutt considers it unnecessary to convert the total fatty acids into lead salts; he therefore recommends the following modification of *Renard's* process:—Dissolve the fatty acids obtained from 10 grms. of oil [by decomposing the saponified mass with hydrochloric acid under ether and evaporating off the solvent] in 50 c.c. of 90 per cent alcohol, add to the solution, which must not be allowed to cool below 38° (to prevent separation of crystals) 5 c.c. of a 20 per cent aqueous solution of lead acetate, cool to about 15° C., agitate, allow to stand for half an hour, filter and wash once with ether. Return the soaps into the flask with the help of ether, digest with ether and repeat

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[1] *Journ. Soc. Chem. Ind.* 1898, 1124.

this operation three times; the lead oleate will thus be entirely dissolved out. Transfer the solid soap with the help of ether into a separating funnel, decompose with hydrochloric acid and wash the ethereal layer free from mineral acid. Distil off the ether, dry the fatty acids in the hot water oven, and pour into the flask 50 c.c. of alcohol of exactly 90 per cent (spec. grav. 0·8340). Dissolve the fatty acids by warming the (corked) flask, and then allow to cool to either 15° C. or 20° C. Collect the crystals on a small filter, or better on a *Gooch* crucible, and wash three times with 10 c.c. of 90 per cent alcohol, each time at the same fixed temperature. The filtrate and washings are measured; the necessary corrections are found in the table given above.

The crystals are thoroughly washed with 70 per cent alcohol, in which the crude arachidic acid is quite insoluble, until the washings remain clear on adding water. It is not necessary, although advisable, to redissolve the acids in 50 c.c. of 90 per cent alcohol and repeat the operations just described. The crystals are dissolved in boiling ether and weighed after drying at 100° C. The correction is then added to the weight. The melting point of the mixed arachidic and lignoceric acids so isolated varied (by capillary tube) from 71° to 72·5° C., but even when working in exact accordance with *Tortelli* and *Ruggeri's* directions the melting point 74°-75° C. could not be obtained by *Archbutt*, the highest figure being 73·3° C. [It may be added that after recrystallising the acids repeatedly from 90 per cent alcohol the melting point was raised to 79·6° C.]

The following table shows in greater completeness the results obtained by *Archbutt* with one and the same sample of arachis oil:—

Estimations of Arachidic and Lignoceric Acids by different Methods in the same Sample of Arachis Oil.

Weight of Oil taken.	Method.	Volume of Alcohol. Temperature, °C. Solubility Coefficient.	Arachidic and Lignoceric Acids.				
			Dissolved in the Alcohol.	Weighed.	Total.	Per cent.	Melting Point by Capillary Tube.
Grms. 10	Renard's; 2 grms. $Pb\bar{A}_2$ aq.; not recrystallised	70 c.c. 20° 0·082	0·0574	0·4283	0·4857	4·86	°C. 71
10	Renard's; 4 grms. $Pb\bar{A}_2$ aq.; not recrystallised	70 c.c. 20° 0·082	0·0574	0·4258	0·4832	4·83	71
10	Renard's; 1 grm. $Pb\bar{A}_2$ aq.; not recrystallised	80 c.c. 15° 0·0625	0·0500	0·4480	0·4980	4·98	71
10	Renard's; 2 grms. $Pb\bar{A}_2$ aq.; not recrystallised	90 c.c. 15° 0·063	0·0567	0·4554	0·5121	5·12	70
10	Renard's; 1 grm. $Pb\bar{A}_2$ aq.; recrystallised	130 c.c. 15° 0·061	0·0793	0·3931	0·4724	4·72	71
10	Renard's; 1 grm. $Pb\bar{A}_2$ aq.; recrystallised	135 c.c. 15° 0·061	0·0823	0·4125	0·4948	4·95	72
20	Tortelli's; exactly as described in *Chem. Zeit.* 1898, 600	265 c.c. 17·5° 0·079	0·2094	0·6935	0·9029	4·51	72
20	Renard's; 2 grms $Pb\bar{A}_2$ aq.; recrystallised; Gooch filter used	250 c.c. 15° 0·070	0·1750	0·7649	0·9399	4·70	72·5
20	Renard's; 2 grms. $Pb\bar{A}_2$ aq.; recrystallised; Gooch filter used	240 c.c. 15° 0·070	0·1680	0·7718	0·9398	4·70	72 72·8-72·3 (Bensemann)
20	Tortelli's; exactly as described; Gooch filter used	248 c.c. 15° 0·069	0·1711	0·6967	0·8678	4·34	72 72·3-73·3 (Bensemann)

This table may be supplemented by the following one showing the accuracy attainable in a practical case.

Results of Analysis of Mixtures of Olive Oil and Arachis Oil

Composition of Oil taken.		Volume of 90 per cent Alcohol. Temperature. Solubility Coefficient.	Arachidic and Lignoceric Acids.					Arachis Oil found.
Olive Oil.	Arachis Oil.		Dissolved in the Alcohol.	Weighed.	Total.	Per cent.	Melting Point.	
Per cent.	Per cent.						C.	Per cent.
...	100	80 c.c. 15° 0·0625	0·0500	0·4480	0·4980	4·98	71	...
90	10	73 c.c. 15° 0·033	0·0241	0·0265	0·0506	0·506	71	10·2
80	20	73 c.c. 15° 0·033	0·0241	0·0715	0·0956	0·956	71	19·2

Tortelli and *Ruggeri*[1] maintain, however, that their modification is less cumbersome and leads to more correct results than the one suggested by *Archbutt.*

The determination of the crude arachidic acid is of the greatest importance in the examination of olive oils suspected of being adulterated with arachis oil, for arachis oil so closely resembles olive oil that judiciously prepared mixtures cannot be detected with certainty by means of the quantitative reactions. For although, as a rule, arachis oil has a higher iodine value than olive oil, a comparison of the numbers given in the table of constants for arachis and olive oils will show that there are arachis oils in commerce the iodine values of which approach closely those of olive oils having exceptionally high iodine values. The quantity of arachin naturally occurring in olive oil is too small to invalidate the correctness of the method. Nor would an admixture of rape oil seriously interfere with the information furnished by *Renard's* test, as special experiments, made in my laboratory, have shown. These experiments have been confirmed by *Archbutt's* determination of the arachidic acid in rape oil.

Adulterants of arachis oil are poppy seed, sesamé, cotton seed, and rape oils.

Poppy seed oil is indicated by a high iodine value and specific gravity of the sample.

Sesamé oil is recognised by the furfural reaction. It has been pointed out already above that a very faint *Baudouin* colour reaction need not necessarily indicate adulteration. In doubtful cases it is advis-

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[1] *Moniteur Scientif.*, 1902 [4], 215; cp. also Perrin. *Moniteur Scientif.*, 1901 [4], 320.

able to determine the iodine value of the oil, as also of its liquid fatty acids, and the solidifying point of the mixed fatty acids.

Cotton seed oil is detected by the same quantitative reactions; the colour reactions described above (p. 530) will serve as confirmatory tests.

Rape oil would be revealed by a lower saponification value of the oil than the normal one, and by low solidifying and melting points of the mixed fatty acids.

Very large quantities of arachis oil are expressed in the South of France; considerable quantities are also prepared in Holland. In this country as yet no arachis oil is made. It has been pointed out already that the oils of first expression are used as salad oils. They are largely employed for adulterating, or even wholly substituting, olive oils. The oils of second and third expression are chiefly used in soapmaking. The chief characteristic component of the Marseilles white soap is arachis oil.

RICE OIL[1]

French—*Huile de riz.* German—*Reisoel.* Italian—*Olio di riso.*

Physical and Chemical Constants of Rice Oil

Specific Gravity.			Saponification Value.		Reichert-Meissl Value.		Iodine Value.	
At °C.		Observer.	Mgrms. KOH.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.
99 (water 99 = 1)	0·8907	Browne	193·2 193·5	Smetham Browne	1·1	Browne	96·4 91·65	Smetham Browne

Physical and Chemical Constants of the Mixed Fatty Acids

Melting Point. °C.	Mean Molecular Weight.	Observer.
36	289·3	Browne

This oil, as obtained in this country from Rangoon rice meal by hydraulic pressure, had a dirty greenish colour. Rangoon rice meal contains about 15 per cent of oil, common rice meal only 8-9 per cent.

The oil obtained from fresh rice bran is practically neutral, but on standing, the proportion of free fatty acids very rapidly increases

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[1] Smetham, *Journ. Soc. Chem. Ind.* 1893, 848.

owing to the action of an enzyme, as has been shown by *Browne*.[1] Thus the oil examined by *Smetham* contained from 31·6-72·2 per cent, and the specimen examined by *Browne* 83 per cent of free fatty acids. This fact explains the high melting point of a commercial oil, viz. 24° C. observed by *Browne*.

The existence of an enzyme in the rice bran was demonstrated by *Browne*, by mixing 20 c.c. of a 20 per cent cold aqueous extract of rice bran with an equal volume of castor oil. After twenty-four hours the emulsion became acid, and after one week the proportion of free fatty acids had risen to 16 per cent. It appears to me not unlikely that the action of the lipase had been arrested in this experiment, since *Browne* had rendered the mixture faintly alkaline to litmus. Further proof of the view that the production of free fatty acids is due to an enzyme was given by an experiment, in which freshly ground rice bran was divided into two portions, one of which was heated to 100° C. to destroy the enzyme. After one month the oil was extracted from both samples. The results of this experiment are reproduced in the following table:—

	Free Acid as Oleic Acid. Per cent.
Raw rice (stored many months)	6·9
Fresh bran (six hours after grinding)	12·5
Bran, one month old, unheated	62·2
,, ,, heated	24·0

TEA SEED OIL

French—*Huile de thé*. German—*Theesamenoel*. Italian—*Olio di thè*.

For table of constants see p. 613.

Tea seed oil is the oil obtained from the seeds of the tea plant *Camellia theifera*; the oil is expressed on a large scale in China; the first pressed oil serves there as an edible oil, although the proportion of saponin it is said to contain renders it somewhat unsafe for consumption. The oil obtained by extraction with solvents is perfectly free from saponin;[2] the lower qualities are used as burning oil and for soapmaking. There are two varieties, viz. Chinese and Assam oil. Chinese tea seed yields 30-35 per cent, Assam tea seed 43-45 per cent of oil.

Tea seed oil is a straw or amber coloured oil, closely resembling olive oil; like the latter it gives a hard elaïdin. The proportion of liquid fatty acids determined by the lead-salt-ether method was found by *Lane* in two samples of tea seed oil 88 per cent and 93·2 per cent respectively.

Similar to this oil is the fatty oil from *Camellia oleifera*, a plant largely cultivated in China for the sake of the pale bland oil prepared from its seeds. Its specific gravity is 0·9175 at 15° C.

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[1] *Journ. Soc. Chem. Ind.* 1903, 1137.

[2] Weil, *Arch. d. Pharm.* 239, 363.

Physical and Chemical Constants of Tea Seed Oil

	Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Hehner Value.		Refractive Index. Oleo-refractometer.	
	At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	Per cent.	Observer.	"Degrees."	Observer.
Chinese oil	15	0· 17-0·927	Schaedler	−5	Schaedler	195·5	Davies	88	Itallie			+8 at 22° C.	Pearmain
Assam oil	15	0·920	Itallie[1]	−12	Itallie	194	Itallie	90·49	Lane	91·5	Itallie		
Japanese oil	20	0·9110	Wijs[2]			188·3	Wijs	88·9	Wijs				

[1] *Journ. Soc. Chem. Ind.* 1894, 79.

[2] *Zeit. f. Unters. Nahrgs. und Genussm.* 1903, 492.

Physical and Chemical Constants of the Mixed Fatty Acids.

Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.	
°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.
10-11	Wijs	195	Wijs	287·6	Wijs	90·8	Wijs
						Liquid Fatty Acids.	
						99·6-104·4[1]	Lane

[1] Calculated.

PISTACHIO OIL[1]

French—*Huile de pistache.* German—*Pistazienoel.*
Italian—*Olio di pistacchio.*

Physical and Chemical Constants of Pistachio Oil

Spec. Grav.	Solidifying Point.	Saponification Value.	Iodine Value.	Maumené Test.
At 15° C.	°C.	Mgrms. KOH.	Per cent.	°C
0·9185	−8 to −10	191·0-191·6	86·8-87·8	44·5-45

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.	Melting Point.	Iodine Value.
°C.	°C.	Per cent.
13 14-13	17-18 18-20	88·9

This oil is contained in the seeds of the pistachio nuts (from *Pistacia vera* or *P. lentiscus*). Oil obtained by extraction with ether has a more pronounced aromatic odour than oil expressed in the cold. The oil has very limited commercial application; it is used in the manufacture of sweetmeats.

HAZELNUT OIL

French—*Huile de noisette.* German—*Haselnussoel.*
Italian—*Olio di nocciuole.*

For tables of constants see p. 616.

Hazelnut oil is prepared from the seeds of the hazelnut tree. *Corylus Avellana*, by pressing or by extracting with solvents. The seeds, contain from 50-60 per cent of oil.

This oil has a golden-yellow colour; it is transparent, and has the odour of hazelnuts. For want of better methods this characteristic odour must be used for its detection in other oils.

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[1] De Negri and Fabris, *Annali del Lab. Chim. delle Gabelle*, 1893, 220.

According to *Hanus*,[1] hazelnut oil consists of 85 per cent of oleic acid, 9 per cent of palmitic acid, and 1 per cent of stearic acid. The iodine value of the liquid acids as found by *Tortelli* and *Ruggeri* points, however, to the occurrence of linolic acid in hazelnut oil. In the elaïdin test it yields a solid white mass.

The specimen examined by *Hanus* contained 0·5 per cent unsaponifiable matter, which was identified as phytosterol. The acetyl value was 3·2.

Hazelnut oil much resembles almond oil; the lower iodine value and the lower solidifying point may serve as means to distinguish the two oils.

Hazelnut oil is used in perfumery, and as lubricating oil for watch springs and other delicate machinery. According to *Filsinger*[2] it is also used in the adulteration of chocolate fats. Hazelnut oil, in its turn, is liable to adulteration with olive oil; the latter would be detected by a high solidifying point of the sample.

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[1] *Chem. Ztg.* 1899, Rep. 226.

[2] *Journ. Soc. Chem. Ind.* 1893. 51.

Physical and Chemical Constants of Hazelnut Oil

Specific Gravity.		Solidifying Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Hehner Value.		Maumené Test.	
At 15° C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.
0·9170	Massie	−20	Girard	197·1	Filsinger	88	Girard	0·99	Schoettler	95·5	Schoettler	35-36	De Negri and Fabris
0·9146	Filsinger	−10	Braconnot	192·8	De Negri and Fabris	88·5	Filsinger	0·99	Hanus	95·6	Hanus	36·2	Hanus
0·9170	De Negri and Fabris			191·4	Soltsien	86·2-86·8	De Negri and Fabris						
0·9164	Soltsien			187	Schoettler	83·2	Soltsien						
0·916	Schoettler			193·7	Hanus	87	Schoettler						
0·9169	Hanus					90·2	Hanus						
						83·9	Tortelli and Ruggeri						

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
9	Soltsien	17	Soltsien	200·6	Hanus	90·1	De Negri and Fabris
		25	Girard				
19-20	Schoettler	22-24	De Negri and Fabris			90·6	Hanus
						Iodine Value of the Liquid Fatty Acids.	
						91·3	Hanus
						97·6	Tortelli and Ruggeri

KOËME OIL[1]

French—*Huile de noix d'Inhambane.*
German—*Koëmeoel, Thalerkürbisoel (Telfairiaoel).*[2]

This oil is obtained from the seeds of *Telfairia pedata*, Hook, a cucurbitacea, indigenous in South-East Africa. The seeds are known in commerce as "Koëme de Zanzibar"; they contain 33 per cent of oil.

Physical and Chemical Constants of Koëme Oil

Specific Gravity.	Solidifying Point.	Saponification Value.	Iodine Value.	Refractive Index.	
At 15 °C.	°C.	Mgrms. KOH.	Per cent.	Butyro-refractometer.	
0·9180	+7	174·8	86·2	At °C.	Scale Divisions.
				25	63-64
				30	61-62

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.	Melting Point.
°C.	°C.
41	44

The oil gives the elaidin reaction; on exposure to the atmosphere for several months it becomes slightly viscous.

The mixed fatty acids contain stearic, palmitic, and telfairic (p. 113) acids, and possibly an unsaturated hydroxylated acid of the composition $C_{24}H_{40}O_3$. The acetyl value of the oil, viz. 26·9 found by *Thoms* is due to the presence of the hydroxylated acid. The remarkably low saponification value of the oil would seem to point to the presence of an acid of high molecular weight.

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[1] Thoms, *Arch. d. Pharm.* 238 (1900), 48.

[2] Cp. *Jahrb. d. Chemie*, ix. 354.

ELDERBERRY OIL

French—*Huile de sureau.* German—*Holunderoel.*
Italian—*Olio di sambuco.*

For tables of constants see p. 619.

This oil is obtained from the berries of the red elderberry, *Sambucus racemosa.*[1] A variety of the same oil was prepared by *Byers* and *Hopkins* from the berries of *Sambucus racemosa arborescens.*[2]

The solid fatty acids of elderberry oil consist, according to *Byers* and *Hopkins*, of palmitic acid exclusively. *Zellner* found in his specimen, besides the chief constituent palmitic acid, small amounts of arachidic acid.

The liquid fatty acids amount, according to *Byers* and *Hopkins*, to 73·6 per cent of the mixed fatty acids, which agrees fairly well with the figure 71 per cent found by *Zellner*. The distinct *Reichert-Meissl* value points to notable amounts of volatile fatty acids. *Byers* and *Hopkins* arrive at the following composition of the oil: palmitin, 22 per cent; olein and linolin, 73·6 per cent (of which olein forms 92·2 and linolin 7·8), caprin, caproin, and caprylin, 3·0 per cent.

Zellner concludes from the iodine value of the liquid fatty acids, viz. 120, that about two-thirds consist of oleic acid and the remainder of linolic acid; linolenic and isolinolenic acids could not be detected.

The specimen of oil examined by *Byers* and *Hopkins* contained 0·66 per cent of unsaponifiable matter, and had the acid value 13·3. The acid value of *Zellner's* specimen was 3·2, the acetyl value 15·5; the mean molecular weight of the acetylated acids was 286, and their melting point 47°-49° C.

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[1] Zellner, *Monatshefte f. Chemie*, 1902, 937. *Journ. Soc. Chem. Ind.* 1903. 101.

[2] H. G. Byers and P. Hopkins, *Journ. Amer. Chem. Soc.* 1902. 771.

Physical and Chemical Constants of Elderberry Oil

Specific Gravity.		Solidifying Point.		Melting Point.		Saponific. Value.		Iodine Value.		Reichert-Meissl Value.		Helmer Value.		Refractive Index.	
At 15°C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	At 20°C.	Observer.
0·9072	Byers and Hopkins	− 8	Byers and Hopkins	0	Byers and Hopkins	209·3	Byers and Hopkins	81·44	Byers and Hopkins	1·54	Byers and Hopkins	91·75	Byers and Hopkins	1·472	Zellner
0·9171	Zellner	− 3 to − 4	Zellner			196·8	Zellner	89·5	Zellner	1·8	Zellner	95 [1]	Zellner		
								110·6	Lewkowitsch	1·3	Lewkowitsch				

[1] This appears to be too high, in view of the Reichert-Meissl value found by the same observer.—(J. L.)

Physical and Chemical Constants of the Mixed Fatty Acids

Melting Point.		Neutralisation Value.		Iodine Value.	
°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
38	Byers and Hopkins	204·8	Zellner	93	Zellner
43	Zellner			Liquid Fatty Acids.	
				120	Zellner

OLIVE OIL

French—*Huile d'olive.* German—*Olivenoel.* Italian—*Olio d' oliva.*

For tables of constants see pp. 621-623.

Olive oil is prepared from the fruits of the olive tree, *Olea europæa sativa*, by the mixed method, *i.e.* by expression and subsequent extraction. The proportion of oil in the fruits varies from 40-60 per cent. In the determination of the proportion of oil in olives or olive pulp, carbon bisulphide should be used in preference to ether, as the latter dissolves other (non-fatty) substances together with the oil.[1]

The specimens of olive oil found in commerce vary to a considerable extent, their quality depending on many circumstances, such as the variety of the olive tree itself [Italy alone produces about 300 varieties of the olive tree], the degree of ripeness of the fruit, the manner of gathering it, the mode of expressing, etc. The very finest oils are prepared from handpicked fruits by crushing in a mill without breaking the kernels, and expressing the marc in a hydraulic press. The oil so obtained—"Virgin oil"—ranks as the best edible oil. "Provence oil" and "Aix oil" are sold as the finest brands, to which comes next in quality the oils sold in this country as "Finest Tuscan cream." A somewhat inferior quality, obtained by pouring some water on the marc and pressing again, is also used as salad oil. The next lower grade oil is prepared by taking the pulp out of the press, mixing it with hot water and pressing again once or twice. Thus the bright oils used for lubricating, soap-making, and other technical purposes—"lavate" oils—are obtained. In large establishments the kernels are separated from the pulp, but in small works the pulp is crushed together with the kernels. Lower grades still, partly obtained by extraction of the press residues ("sanza") with solvents (carbon bisulphide or petroleum ether), are sold under the name of *huiles de ressence*, *huiles d'enfer* (from marc fermented in pits), *sottochiari*, *sulpho-carbon oils*, *sulphur olive oil*, etc. "*Tournant oil*" is a commercial product of the quality of the "*huiles d'enfer*," obtained from the fermented marc of expressed olives; it contains a considerable quantity (up to 26 per cent) of free fatty acids, and, therefore, forms a very complete emulsion with a solution of sodium carbonate, which constitutes its value as Turkey-red oil (Chap. xv.). Still lower qualities contain more free fatty acids. Thus a sample of "olive oil grease" examined in the writer's laboratory had 48 per cent of free fatty acids; some Ligurian and Sardinian sulphur olive oils were found to contain 46 and 57 per cent of free fatty acids respectively (cp. Chap. v. p. 171). Portuguese oils obtained from fermented marc ("bagassa") reach even the high figure 60 and 70 per cent of free fatty acids; this is due, no doubt, to the somewhat primitive fashion[2] of treating the olives; hence the ferments contained in them produce a high degree of natural hydrolysis (see footnote, p. 625).

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[1] Cp. Peano, *Journ. Soc. Chem. Ind.* 1903, 35.

[2] Klein, *Zeit. f. ang. Chemie.* 1898, 848; Mastbaum, *Chem. Rev.* 1904. No. 3.

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Reichert Value.	
At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. 1/10 norm. KOH.	Observer.
12	0·9192	Saussure	At 2 turbid, at 6, "stearine" separates	Chateau	191-196	Allen	82·8	Hübl	0·3	Medicus and Scheerer
15	0·9177	,,	+3 to +4[8]	Bertainchaud	188·7-203[1]	Dieterich	81·6-84·5	Dieterich	Reichert-Meissl Value.	
15	0·9178[1]	Clarke	+9 to +10[9]	,,	185-196[3] generally 190	De Negri and Fabris	79·18-82·3	Villavechia	0 6	Crossley and Le Sueur[5]
15	0·9196[2]	,,			190·5-195[10]	Oliveri	79-88[3] generally 82	De Negri and Fabris		
15	0·916-0·918[3]	De Negri and Fabris			190·9[5]	Crossley and Le Sueur	79-83·2[10]	Oliveri		
15·5	0·9141-0·9171	Thomson and Ballantyne			189·3-194·6[4]	Tolman and Munson	78·9-86·9	Thomson and Ballantyne		
15·5	0·91747-0·91797[4]	Moerck					77·28-88·68[4]	Lengfeld and Paparelli		
15·5 (water at 15·5 = 1)	0·9203	Crossley and Le Sueur[5]					80·7-91·5[11]	Guozdenovič		
15·5	0·9155-0·9180[6]	Tolman and Munson					83·3-86·1[12]	Ferreira da Silva		
15·5	0·9162-0·9180[7]	,,					93·67[5]	Crossley and Le Sueur		
18	0·9144-0·9163	Stilurell					78·6-87·2[13]	Tortelli and Ruggeri		
18	0·9139-0·9141	Long					84·0[14]	,,		
19	0·9134	,,					79·1[15]	,,		
20	0·9127	,,					87-87·5[16]	Ahrens and Hett		
21	0·9119-0·9121	,,					91·4-91·7[17]	,,		
22	0·9112-0·9114	,,					85·1[4]	Tolman and Munson		
23	0·9106-0·9117	,,					81·5[18]	,,		
23	0·912-0·914	Dieterich					82·8[19]	Shukoff		
24	0·9101-0·9099	Long					85[20]	,,		
25	0·9094	,,								
30	0·9060	,,								
35	0·9028	,,								
50	0·8932	Saussure								
94	0·8625	,,								

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[1] "Virgin oil." [2] Gallipoli oil. [3] Derived from observations on 203 samples. [4] Californian oils. [5] Oil from the Punjab. [6] 18 Italian oils. [7] 38 Californian oils. [8] Tunisian oils from the South (Gabès, Safsa, Djerba). [9] Tunisian oil from Sfax (cp. p. 625). [10] Derived from observations on 106 samples. [11] 60 samples of Dalmatian oils (in one case even 92·8 was found). [12] Portuguese oils. [13] Spanish oils. [14] Greek oil. [15] Turkish oil. [16] *Chem. Repert.* 1903, 241. Morocco oil from green olives. [17] Morocco oil from black olives. [18] Italian oils. [19] Crimean. [20] Persian.

Physical and Chemical Constants of Olive Oil—continued

Hehner Value.		Thermal Tests.				Refractive Index.			Viscosity in Redwood's Viscosimeter.	
		Maumené Test.		Heat of Bromination.						
Per cent.	Observer.	°C.	Observer.	°C.	Observer.	At °C.		Observer.	Seconds at 70° F.	Observer.
95·43	West-Knight	41·5-45·5	Archbutt	15	Hehner and Mitchell	15	1·4698	Strohmer	312·3[1]	Crossley and Le Sueur
94-96[4]	Lengfeld and Paparelli	35[2,3] (mean)	De Negri and Fabris			15	1·4703[5]	Guozdenovič		
		45-47[4]	Blasdale	14·3	Jenkins	15·5	1·4703-1·4713[4,3]	Tolman and Munson		
95·14[1]	Crossley and Le Sueur			13·55 to 14·5	Archbutt	20	1·4670-1·4705	Holde		
						60	1·4548	Thoerner		
		Specific Temperature Reaction.				Oleo-refractometer.				
		89-95	Thomson and Ballantyne			“ Degrees.”		Observer.		
						0 to 2		Jean		
						0 to +1·5		Bruyn and van Leent		
						+1 to +3·5[6] at 22° C.		Pearmain		
						Butyro-refractometer.				
						At° C.		Observer.		
						15·5	67·3-68·5[7]	Tolman and Munson		
						15·5	66·9-69·2[4]	,,		
						25	62-62·8	Mansfeld		
						40	54·13-54·7	Bömer		
						40	56·4[1]	Crossley and Le Sueur		

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[1] Oil from the Punjab. [2] Derived from observations on 203 samples. [3] By Jean's thermeleometer. [4] Californian oils. [5] 60 samples of Dalmatian oils (in one case the iodine value was 92·8). [6] 105 samples. [7] Italian oils.

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.			Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.		Refractive Index.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.	At 60° C.	Observer.
99 (water 15·5=1)	0·8430	Allen	21·2	Hübl	26	Hübl	193	Thoerner	279·4	Allen	86·1	Morawski and Demski	1·4410	Thoerner
			21	Allen	26	Allen			286	Williams				
100 (water 100=1)	0·8749	Archbutt	Not below 22	Bach	23-24 to 26-27	Bensemann					90·2	Williams		
											87-88	Thoerner		
			23·5-24·6	Dieterich	26·5-28·5	Bach								
			22-17[1]	De Negri and Fabris	24-27[1]	De Negri and Fabris					Iodine Value of the Liquid Fatty Acids.		Refractive Index of the Liquid Fatty Acids.	
			21-22	Thoerner	19-23[5]	Moerck								
					Mostly below 28[5]	Lengfeld and Paparelli								
			Titer Test.		26-28	Thoerner					96·4-97	Bömer	Butyro-refractometer.	
					21-26[5]	Blasdale[6]					92·8[5]	Tolman and Munson		
					21·6-29·3[7]	Tolman and Munson								
			16·9-17·15		19·2-31·0[5]	,,					94·0[7]	,,	At 40° C.	
			17·1-17·8 [2]								95·5-101·5[8]	Tortelli and Ruggeri		
			18·6-19·7	Lewkowitsch										
			19·45-20								95·5-104·2[9]	,,	42·7	Bömer
			23-25								103·5[10]	,,		
			20·1-21·2 [3]								96·3[11]	,,		
			19·75-20·8	,,										
			21-21·87											
			21·5-22·9											
			18·4-19·2											
			18·9-19·8											
			25·2-26·4[4]	,,										

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[1] Derived from observations on 203 samples. [2] Finest Tuscan cream. [3] Commercial oil. [4] Gallipoli oil. [5] Californian oils. [6] *Journ. Soc. Chem. Ind.* 1896, 206. [7] Italian oils. [8] 12 Italian oils, iodine values varied from 80·0 to 85·4. [9] 7 Spanish oils, iodine values varied from 78·6 to 87·2. [10] Greek oil, iodine value 84·0. [11] Turkish oil, iodine value 79·1.

In recent years California has become a very important producer of olive oil; the production of oil in South Australia is also rapidly increasing.[1]

The **colour** of olive oil varies considerably; the commercial oils are of all shades from colourless to golden-yellow; a green colour is very pronounced in the low-class olive oils, due to dissolved chlorophyll.

The **taste** of olive oil in its purest state is bland and pleasant; it varies, however, with the locality where the fruit has been grown. Thus, the oils obtained from Tuscan fruits possess a decidedly more agreeable taste than those from Ligurian olives. Therefore purity alone is not a sufficient test in the valuation of a sample of olive oil. An oil may be free from adulteration and still be an inferior oil, on account of its rank and nauseous taste. *Canzoneri*[2] isolated from the bitter and harsh Puglia olive oils eugenol, to which he ascribes the harsh taste, and further catechol, gallic acid, tannin, and an unknown substance, which latter are said to cause the bitter taste. It is noteworthy that the objectionable taste disappears in time. The large quantities of edible oils produced in Tunis[3] are frequently admixed with the best brands of French and Italian edible oils, in order to mask their somewhat harsh taste.

The solid fatty acids of olive oil consist of palmitic and a minute proportion of arachidic acid. *Hehner* and *Mitchell*[4] did not obtain any stearic acid crystals from olive oil, therefore absence of stearin must be taken as proven.

Recently *Tolman* and *Munson*[5] found in the examination of eighteen samples of genuine Italian olive oils as the lowest amount of solid fatty acids obtainable by the lead-salt-ether method 5·0 per cent (in a Tuscany oil of the iodine value 80·7), and as the highest amount 17·72 per cent (in a Bari oil of the iodine value 81·2), whereas in the corresponding examination of thirty-eight Californian olive oils the lowest amount found was 2·0 per cent of solid fatty acids (in a Santa Barbara oil of the iodine value 84·7), and the highest amount 12·96 per cent (in a Cloverdale oil of the iodine value 81·9).

These numbers seem to be somewhat conflicting, but they dispose finally of the older statement that olive oil contains, as a rule, about 28 per cent of solid glycerides.

Tunisian oils from Sfax contain, according to *Bertainchaud*,[6] 25 per cent of solid fatty acids. The high amount of solid glycerides causes these oils to deposit "stearine" at + 9° to + 10°. The difference in composition as regards solid fatty acids of the various kinds of Tunisian oils is exemplified by the following table:—

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[1] In 1902 there were in the colony 66,852 olive-trees, which yielded 11.327 gallons of oil (1901, 6520 gallons).

[2] *Gaz. Chim. Ital.* 27. ii. 1.

[3] With regard to the Tunisian olive oil industry compare Milliau, Bertainchaud, and Malet, *Monit. Scient.* 1900, 56 [704], 508.

[4] *Analyst*, 1896, 328.

[5] *Journ. Amer. Chem. Soc.* 1903, 956.

[6] *Bull. de la direction de l'agric. et du comm.* Tunis. viii. (1903), 167.

	Solid Fatty Acids.	Liquid Fatty Acids.
	Per cent.	Per cent.
Olive oil from the North (Tunis, Bizerte, Cap-Bon, Medjerdah)	15	85
Oil from the Centre (Sousse, Mahdia, Monastir)	21	79
Oil from Sfax	25	75
Oils from the South (Gabès, Safsa, Djerba)	15	85

In order to free the Sfax oils from the excess of glycerides of solid fatty acids, it is necessary to "demargarinate" them (cp. chap. xv.).

The liquid glycerides were formerly considered to be practically pure olein (notwithstanding a conjecture of *Mulder's* as to the presence of an unsaturated fatty acid other than oleic), but *Hazura* and *Grüssner* have shown that the liquid portion of olive oil contains, besides oleic acid, the less saturated linolic acid (approximately in the proportion of 93 oleic acid to 7 linolic acid). From this proportion the iodine value of the liquid fatty acids would be found by calculation = 96·56; this number is in agreement with most of the numbers found experimentally.

The *minimum* iodine value of the liquid fatty acids in the above-mentioned eighteen Italian olive oils, examined by *Tolman* and *Munson*,[1] was 89·8 [2] (Tuscany oil of the iodine value 80·7), and the *maximum* 98·4 (in an Abruzzi oil containing 13·51 per cent of solid fatty acids). The lowest iodine value of the liquid fatty acids of the thirty-eight Californian olive oils was 88·9 (in a Napa oil of second expression), and the highest iodine value of the liquid fatty acids 99·6 (in a Chico oil containing 5·12 per cent of solid fatty acids).

Holde and *Stange*[3] obtained 1-2 per cent of oleodimargarin on allowing an ethereal solution of olive oil to crystallise at − 40° to − 45° C.

The amount of **free fatty acids** in commercial olive oils varies with the care observed in their preparation; in order to prevent hydrolysis[4] the oil must be separated as carefully as possible from the putrescible marc. Once hydrolysis has set in, olive oil, like other oils, becomes rancid when exposed to the atmosphere. From a very rancid olive oil *Scala*[5] isolated œnanthylic aldehyde, formic, acetic, butyric, œnanthylic acids, also azelaic and suberic acids (cp. p. 25). The acetyl value of an old commercial oil was found = 10·6 by *Lewkowitsch*. In the following table some published results are tabulated :—

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[1] *Journ. Amer. Chem. Soc.* 1903, 956.

[2] This number does not necessarily point to the absence of linolic acid, since the "liquid" fatty acids very likely contained some saturated fatty acids.

[3] *Berichte*, 1901, 2406.

[4] It is very likely that the hydrolysis is due to the action of a ferment. Indeed, *Tolomei* (*Atti dei Linc.* 1896) ascribes to a ferment, "olease," the fermentation which readily is set up in the stored marc.

[5] *Staz. Sper. Agr. Ital.* 30. 613.

Free Fatty Acids in Olive Oil

Description of Sample.	Number of Samples.	Free Fatty Acids as Oleic Acid. Per cent.	Observer.
...	1	1·17	Salkowski
...	1	1·66	Rechenberg
Commercial oil . .	49	Less than 5	Archbutt
,, ,, . .	66	5-10	,,
,, ,, .	44	10-15	,,
,, ,, . .	1	20-25	,,
,, ,, . .	11	3·86-11·28	Thomson and Ballantyne
,, ,, (Syrian)	1	23·88	,,
,, ,, (Californian)	3	1·55-8·33	Moerck
,, ,, (European)	3	0·97-1·09	,,
,, ,, (Italian)	18	0·57-2·79	Tolman and Munson
,, ,, (Californian)	38	0·20-3·51	,,

Olive oils containing more than 5 per cent of free fatty acids are not suitable for lubricating purposes; they are also unsuitable for burning, as they cause charring of the wick.

The **unsaponifiable matter** in olive oil, as in all vegetable oils, is phytosterol. *Thomson* and *Ballantyne* found in 12 samples of oil the proportions of unsaponifiable matter between 1·04 and 1·42 per cent, which is somewhat higher than the *minimum* and *maximum* amounts recorded for a large number of samples, viz. 0·46 and 1·0 per cent respectively.

Olive oil is the type of a non-drying oil. Hence it shows in the *Maumené's* test, as also in the heat of bromination test, of all vegetable oils the smallest rise of temperature, and shows also the lowest absorption of oxygen in *Livache's* test (p. 306). At higher temperatures olive oil spread on lead powder becomes oxidised.

On account of its comparatively high price olive oil is adulterated to an enormous extent. The oils that are usually admixed with it are sesamé, rape, cotton seed, poppy seed, arachis, and lard oils. The olive oils sold under fancy names are, as a rule, adulterated.

The tables of constants contain a very exhaustive list of numbers, so that by carefully scrutinising them, methods for the examination of a given sample, suspected of being adulterated, can be derived. It is therefore only necessary to emphasise the most salient points.

The **specific gravity** of olive oil ranges from 0·914 to 0·917 at 15° C., but may rise to 0·920 in the case of commercial oils expressed at a higher temperature. Oils of high specific gravity usually exhibit a darker colour. The influence of free fatty acids on the specific gravity has been pointed out already (chap. v. p. 171). If the specific gravity of a pale olive oil be found higher than 0·917, it must be looked upon with suspicion, as possibly adulterated with *sesamé, cotton seed*, or *poppy seed oils*. Sophistication with *rape* or *arachis oil* is not indicated by the specific gravity, the differences in their respective gravities being too insignificant.

The **melting and solidifying points of the fatty acids** (or titer test) will also furnish useful indications as to the purity of an olive oil. But it would be hazardous to draw too far-reaching results from this test. Hence the tabulated observations recorded in the second edition of this work have been omitted.

The most important of the **quantitative reactions** is the **iodine test**, constituting, as it does, the most valuable means of detecting adulteration. Olive oil has nearly the lowest iodine absorption of any oil that might be used for adulteration. As a rule, the iodine value of olive oil should be from 81·6 to 84·5. There occur, however, undoubtedly genuine oils, the iodine values of which exceed these numbers. Thus the oil from the Colombaio olive reaches 86, oil from some Portuguese varieties (sevilhana, mançanilha, cordovil) 87 (*Klein*), Californian oils 88, and in the case of a Dalmatian oil as high a figure as 92·8 was obtained (this has been even exceeded by an olive oil from the Punjab showing 93·67). Still these cases are notable exceptions, and an oil with an iodine value exceeding 85 must, as a rule, be looked upon with suspicion.

Paparelli[1] studied the causes of the variability of the iodine values, and arrived at the following conclusions:—The more mature the olives are the higher is the iodine absorption of the oil. Old and rancid oil has generally a slightly lower number than fresh oil. The method of preparing the oil has also its influence. Oil from the pulp absorbs slightly less iodine than that obtained by grinding pulp and "pits" together; oils extracted by solvents show lower values than expressed oils; again, oils from pits are characterised by higher numbers than those extracted from the fruit. The greatest variation, however, is found to be due to the variety of the olive tree from which the fruit is obtained.

If there is reason to exclude abnormal oils, a high iodine absorption may indicate adulteration with as little as 5 per cent of a *drying oil* (poppy seed, hemp seed oil) or 15 per cent of *sesamé*, *cotton seed*, and *rape oils*. Less positive results are obtained in the presence of *arachis oil*, since the lowest values recorded for that oil almost coincide with the highest value observed on olive oil.

It may be pointed out here that the iodine values of the semi-solid and of the liquid portions into which olive oil separates on partial solidification almost coincide (*Goldberg*).[2]

The **saponification value** will only lead to definite results if large quantities of *rape oil* be admixed with the sample.

In the **elaïdin test** olive oil yields of all oils the hardest elaïdin, and also requires the shortest time for solidification. The elaïdin reaction can only be used as a preliminary test. The effect of an addition of rape or cotton seed oil to olive oil is shown in the following table compiled from tables published by *Archbutt*:[3]—

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[1] *Journ. Soc. Chem. Ind.* 1892, 848.

[2] *Ibid.* 1897, 447.

[3] *Ibid.* 1886 308.

Kind of Oil.	Minutes required for Solidification, at 25° C.	Consistence.
Olive oil	230	Hard, but penetrable
Olive oil + 10 per cent of rape oil .	320	Buttery
,, +20 ,, ,, .	From 9 to 11½ hours	
,, +10 ,, cotton seed oil	From 9 to 11½ hours	Very soft butter
,, +20 ,, ,,	More than 11½ hours	

It has been proposed to measure the effect of a foreign oil on the hardness of the elaïdin quantitatively by using *Legler's* method (p. 212), but it should be borne in mind that, according to *Gintl*, olive oil, after exposure to sunlight for a fortnight, no longer gives a solid elaïdin. *Farnsteiner*[1] has shown that the amount of oleic acid that is converted into elaïdic acid depends very much on the conditions under which nitrous acid is acting on the oil. Indeed, when determining the amount of liquid fatty acids that had not been converted into elaïdic acid (by means of the lead-salt-benzene method), so widely differing results were obtained that the hope of basing a quantitative method upon it must be abandoned at present.

The **thermal reactions** lead to lower values than in the case of any other vegetable oil. *Lengfeld* and *Paparelli* assert that there exists a proportionality between the iodine number and the **Maumené test** of various olive oils. They obtained for fourteen oils numbers varying from 33·5° to 41° C., the oil having the highest iodine absorption also causing the greatest rise of temperature. Their results, arranged by the writer according to the iodine values, do not, however, bear out fully the correctness of this rule.

Olive Oil, No.	Iodine Value. Per cent.	Maumené Test. °C.
1	77·28	35
2	78·42	33·5
3	78·51	33·5
4	78·52	34
5	79·50	36
6	79·53	34·5
7	80·80	37
8	81·45	38
9	81·50	35
10	81·70	34
11	83·35	37·5
12	85·44	36·5
13	87·15	41

The proportionality between iodine number and **heat of bromination test** shows in a general way the same regularity, as will be seen from the numbers given in the following table (*Archbutt*[2]) :—

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[1] *Zeit. Unters. Nahrgs. u. Genussm.* 1899, 8.

[2] *Journ. Soc. Chem. Ind.* 1897, 311.

Olive Oil.	Iodine Value. Per cent.	Heat of Bromination. °C.
Malaga	78·4	14·2
...	78·7	13·55
...	78·9	13·8
Malaga	79·3	13·8
...	81·4	14·2
...	81·4	14·35
Gallipoli	82·0	14·4
,,	82·1	14·5
,,	82·5	14·5
...	84·2	14·45

The examination of the **unsaponifiable matter** in olive oil[1] will be required if admixture of lard oil be suspected. The presence of the latter would be unmistakably detected in the phytosteryl acetate test. The alcohol contained in the unsaponifiable matter from olive oil melts at 135·5°-136·5° C. (*Bömer*), 135°-135·5° C. (*Gill* and *Tufts*). Its acetate melts at 120·3°-120·7° C. (*Gill* and *Tufts*).

Green olive oils should be tested for **copper**, some specimens of "*Malaga* oil" being coloured green by admixture with copper acetate. Copper is best detected in the manner described above (p. 153).

In the following lines I collate the most useful tests for the detection of those oils that occur as adulterants in commercial olive oils :—

1. **Arachis Oil.**—Iodine absorption; the amount of iodine absorbed will be, as a rule, higher than that of normal olive oil. *Determination of arachidic acid* (see "Arachis Oil," p. 604).

2. **Sesamé Oil.**—Specific gravity; iodine absorption of the oil and of its liquid fatty acids; and, as most characteristic, *Baudouin's* test as modified by *Villavecchia* and *Fabris* (see "Sesamé Oil," p. 541). In order to avoid errors that might be caused by abnormal oils, such as Tunisian, etc., the liquid fatty acids should be examined.

3. **Cotton Seed Oil.**—Specific gravity; melting point of fatty acids, iodine absorption of the oil, iodine value of the liquid fatty acids. Colour reactions as confirmatory tests (p. 530).

It should be borne in mind that some genuine olive oils give the *Bechi* reaction very distinctly (*Tortelli* and *Ruggeri*); in doubtful cases, the liquid fatty acids should therefore be tested. It should further be remembered that if heated cotton seed oil has been used for adulteration, the *Halphen* and *Bechi* test fail.

As an illustration of how far it is possible to detect adulteration by examining the liquid fatty acids, I give the following table, in which the iodine value of the liquid fatty acids of the mixtures named is calculated for the lowest and highest values of olive and cotton seed oils respectively.

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[1] It should be noted that in Germany olive oil is denatured with rosemary oil, which of course increases the amount of unsaponifiable matter.

Olive Oil.	Cotton Seed Oil.	Iodine Value of Liquid Fatty Acids.			
Per cent.	Per cent.	I.	II.	III.	IV.
100	0	95	95	104	104
95	5	97·6	97·8	106·15	106·35
90	10	100·2	100·6	108·3	108·7
85	15	102·8	103·4	110·45	111·05
80	20	105·4	106·2	112·6	113·4
0	100	147	151	147	151

It will be seen that by this test alone, small quantities of cotton seed oil cannot be detected; the detection by this test alone is rendered still more difficult if arachis oil be present.

4. **Rape Oil.**—Iodine absorption of the oil and the liquid fatty acids; melting and solidifying points of the mixed fatty acids; *saponification value.* With regard to arachidic acid, cp. p. 610.

5. **Castor Oil.**—Specific gravity; *acetyl value;* behaviour with solvents.

6. **Curcas Oil** (used in Portugal, according to *Hiepe*, to adulterate olive oil).—Iodine absorption. Admixtures of even 10 per cent are said to be detected by the intense reddish-brown colouration the sample will assume a short time after treatment with nitric acid and metallic copper (in the elaïdin test).

7. **Lard Oil.**—Melting point of fatty acids; viscosity; odour of lard on warming. *Phytosteryl acetate test.*

8. **Drying Oils.**—Iodine value. Thermal tests. Hexabromide test.

9. **Hydrocarbons.**—Determination of unsaponifiable matter. Adulterants falling under this class are: colourless vaseline and mineral oils.

10. **Fish Oils.**—The detection of fish oil in olive oil is required in the case of olive oil intended for preserving sardines, etc. (Since the body oil of the sardine becomes intermixed with the olive oil used for preserving the fish, fish oils will always be present to some extent in olive oil which has been drawn from the tins containing preserved fish.[1]) Fish oils will be detected by the taste and smell, especially on warming, and notably by the high iodine value of the oil and the isolation of insoluble brominated fatty acids.

When testing a suspected olive oil, it should be borne in mind that the adulterator has kept pace with the progress of our analytical methods, and that, in order to render detection more

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[1] Thus an olive oil of the iodine value 78·9, employed for the tinning of sardines, and taken from the tins after two months, one year, and two years, had absorbed 99·02, 109·05, and 126·2 per cent of iodine respectively.—Klein, *Zeit. angew. Chemie*, 1900, 559. Similarly, an oil of the iodine value 84·9, used in the conservation of sprats taken from the tins after one year, showed the iodine value 97·2.—Henseval and Deny, *Trav. de la Station Maritime à Ostende*, 1903.

difficult, he no longer uses one single oil, but prefers a mixture of several oils. Thus, it has been pointed out by *Jean*[1] that olive oil is frequently adulterated with 8 to 10 per cent of a mixture consisting of equal parts of poppy seed, cotton seed, sesamé, and arachis oils. In a case of this kind, the determination of the iodine value of the liquid fatty acids will furnish the first and most important indication, after the presence of sesamé oil has been ascertained by means of the *Baudouin* test.

Turkey-red oil (Tournant oil) is, as a rule, tested for the percentage of free fatty acids, which should be present to the extent of about 25 per cent, calculated to oleic acid. Adulterants may be detected by the iodine test.

OLIVE KERNEL OIL

French—*Huile de noyaux d'olive.* German—*Olivenkernoel.*
Italian—*Olio di nòccioli d'oliva.*

Physical and Chemical Constants of Olive Kernel Oil

Oil obtained by	Specific Gravity.		Saponification Value.		Iodine Value.		Refractive Index.	
	At 15° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	At 25° C.	Observer.
Expression of fresh kernels	0·9184-0·9191	Klein	182·3-183·8	Klein	86·99-87·8	Klein	1·4682-1·4688	Klein
Drying and subsequent extraction of the once pressed kernel	0·9193	,,	181·2	,,	87·1	,,	1·4673	,,

Olive kernel oil is the oil obtained by pressing or extracting from the seeds contained in the olive stones. What had been formerly described as olive kernel oil was a highly rancid olive oil containing such quantities of olive kernel oil as would be expressed from the seeds on grinding the marc and crushed kernels with water (p. 620);[2] in the second and third expressions. Olive kernel oil obtained by expression in the cold has a golden yellow colour; the oil expressed in the hot possesses a greenish tint, whereas kernel oil extracted with solvents is dark green, no doubt due to the presence of chlorophyll. The taste of the expressed oil is sweetish, somewhat resembling that of almond oil, without, however, exhibiting the characteristic taste of olive oil.

Olive kernel oil contains about 10 per cent of solid fatty acids, amongst which were identified stearic and palmitic acids, but no

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[1] *Annal. de chim. anal.* 1898, 218.

[2] Klein, *Journ. Soc. Chem. Ind.* 1898, 1055.

arachidic acid. The chief constituent of the liquid fatty acids is oleic acid, also small quantities of linolic acid occur in the oil.

The expressed oil in its fresh state is practically free from fatty acids. The oils expressed by *Klein* contained from 1·0 to 1·78 per cent of free fatty acids; the expressed mass, after drying, yielded to solvents an oil containing 30·4 per cent of free fatty acids, owing to decomposition of the glycerides during the prolonged contact of the oil with the organic matter.

The solubility of the oil in alcohol does not materially differ (in contradistinction to former statements) from that of olive oil.

Also in other respects the oil resembles olive oil closely. Olive kernel oil naturally occurs in those olive oils which have been obtained from olive marc crushed with the kernels. *Klein* proved by special experiments that the belief obtaining amongst olive oil growers, viz., that the crushing of the kernels causes olive oil to turn rancid easily, is groundless.

COFFEE BERRY OIL

French—*Huile de café.* German—*Kaffeebohnenoel.*
Italian—*Olio di caffè*

For tables of constants see p. 633.

Coffee berry oil—extracted by means of ether from the coffee berries—has an intense greenish-brown colour; it possesses a faint odour of raw coffee. By roasting the berries the oil is very little changed. According to *Hilger* and *Juckenack*,[1] the loss of oil during the roasting of coffee berries amounts to 9 to 10 per cent; berries glazed with sugar lost about 20 per cent.

The samples examined by *Spaeth* contained from 2·25-2·29 per cent of free acid, calculated as oleic acid.

According to *Hilger*, coffee berry oil consists of olein and small quantities of palmitin and stearin.[2]

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[1] *Analyst*, 1897, 287.

[2] *Chem. Zeit.* 1895, 776 (Hehner and Mitchell's method was not known then).

[Table

Physical and Chemical Constants of Coffee Berry Oil

Specific Gravity.		Solidifying Point.		Saponification Value.		Reichert-Meissl Value.		Iodine Value.		Maumené Test.	Refractive Index.	
At 15° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	° C.	At 25° C.	Observer.
0·9510-0·9525	De Negri and Fabris[1]	5 – 3 6 – 3	De Negri and Fabris	165·1-173·37	De Negri and Fabris	1·65-1·7	Spaeth	85·89-87·34 (78·65)	De Negri and Fabris	53-55[1]	1·4777-1·4778	Spaeth
				176·2-177·3	Spaeth[2]			85·3-86·8	Spaeth		Butyro-refractometer.	
											79-79·25 at 25° C.	Spaeth

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.	Melting Point.	Neutralisation Value.	Iodine Value.
°C.	°C.	Mgrms. KOH.	Per cent.
36 – 34	38-40	172-178	88·82-90·35
...	...	...	(81·8)

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[1] De Negri and Fabris, *Anali del Labor. chim. delle Gabelle*, 1893, 253.

[2] Spaeth, *Chem. Zeit.* 1895, Rep. 292.

UNGNADIA OIL [1]

Physical and Chemical Constants of Ungnadia Oil

Specific Gravity.		Solidifying Point.	Saponification Value.	Iodine Value.	Hehner Value.
At °C.		°C.	Mgrms. KOH.	Per cent.	Per cent.
15	0·9120	−12	191-192	81·5-82	94·12
100	0·8540				

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.	Melting Point.	Iodine Value.
°C.	°C.	Per cent.
10	19	86-87

Ungnadia oil is obtained from the seeds of *Ungnadia speciosa*, a tree indigenous to Texas.

BEN OIL

French—*Huile de ben.* German—*Behenoel.*
Italian—*Olio di ben.*

For tables of constants see p. 635.

Ben oil is prepared from the seeds of the ben nut from *Moringa pterygosperma, s. oleifera.* Genuine ben oil obtained by the author[2] from the Jamaica section of the Imperial Institute, represents at the ordinary temperature a whitish or yellowish-white translucent mass melting about 25° C. Other specimens described in the table of constants are liquid at the ordinary temperature and separate some "stearine" on standing at about 0° C. This oil has a slightly yellowish colour, is odourless, and has a sweet taste.

Ben oil is stated to consist of the glycerides of oleic, palmitic, and stearic acids, and of a solid acid of high melting point; according to *Völcker*,[3] this acid is identical with behenic acid, melting point 76° C. [arachidic acid?].

In the East ben oil serves as a cosmetic; it used to be employed in the "maceration" process for extracting perfumes from flowers. The liquid portion of the oil becomes rancid only after long exposure; therefore this oil is valuable for lubricating watch-springs and other delicate machinery.

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[1] Schaedler, *Pharm. Zeitung*, 1889, 340.

[2] Lewkowitsch, *Analyst*, 1903, 343.

[3] Liebig's *Annalen*, 64, 342.

Physical and Chemical Constants of Ben Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Butyro-refractometer.		
At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.		Observer.
15	0·9120	Chateau	Solidifies completely at 0; deposits crystals at 7	Chateau	185·6[5]	Lewkowitsch	84·1[1,2]	Mills	40	60·5[4]	Lewkowitsch
,,	0·9198[2]	Mills			186·17-	,,	80·8[1,3]	,,	,,	59·0[5]	,,
,,	0·9161[3]	,,			187·7[6]	,,	111·8[4]	Lewkowitsch	,,	50·0[6]	,,
15·5	0·91998[4]	Lewkowitsch			184·6[4]		109·9[5]	,,	,,	59·0[7]	,,
,,	0·91840[5]	,,					72·2[6]	,,			
,,	0·91267[6]	,,	8·8[6]	Lewkowitsch			112·6[7]	,,			

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.	
°C. Titer Test.	Observer.
37·2-37·8	Lewkowitsch

[1] Calculated from bromine value.
[2] Containing much solid fat.
[3] Containing no solid fat.
[4] Freed from "Stearine."
[5] Portion solid at 0°.
[6] Oil from *Moringa pterygosperma.*
[7] Commercial oil.

STROPHANTUS SEED OIL[1]

French—*Huile de strophante.* German—*Strophantusoel.*
Italian—*Olio di strofanto.*

Physical and Chemical Constants of Strophantus Seed Oil

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.	
At °C.		Observer.	C°.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.
13	0·9254	Mjöen[1]					187·9	Mjöen
15	0·9249	Bjalobrzewski[2]	-6	Bjalobrzewski	+2	Bjalobrzewski	194·6	Bjalobrzewski

Physical and Chemical Constants of Strophantus Seed Oil—continued.

Iodine Value.		Reichert-Meissl Value.		Saponification Value.	
Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Mgrms. KOH.	Observer.
73·02	Mjöen	0·5	Mjöen	187·9	Mjöen
101·6	Bjalobrzewski	0·9	Bjalobrzewski	194·6	Bjalobrzewski

This oil is obtained from the seeds of *Strophantus hispidus*, which contain 22 per cent of oil. The oil has a brownish-green colour, appearing yellowish-brown by transmitted light.

The sample examined by *Bjalobrzewski* contained 12 per cent free fatty acids, and traces of a volatile oil. Amongst the volatile acids formic acid was identified; from the insoluble fatty acids oleic, stearic, and arachidic acids were isolated (by fractional distillation of the ethylic esters).

The melting point of the mixed fatty acids was 28-30 C.

TROPÆOLUM OIL[3]

French—*Huile de cresson d'Inde.* German—*Tropaeolumoel.* (*Kapuzinerkressenoel*). Italian—*Olio di tropeolo.*

This oil is obtained from the seeds of *Tropæolum majus*; it is a buttery mass, melting at a temperature slightly above the ordinary.

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[1] Mjöen, *Archiv d. Pharmacie*, 1894 (234), 283.
[2] *Journ. Soc. Chem. Ind.* 1901, 817.
[3] Gadamer, *Arch. d. Pharmacie*, 1899, 273, 472.

On standing, a very considerable portion crystallises from the oil; the crystals consist of pure trierucin.

The iodine value of tropæolum oil is 73·75; since this value differs but slightly from the theoretical number of trierucin—72·2—the oil may be considered as consisting chiefly of trierucin.

PARADISE NUT OIL[1]

French—*Huile de noix de paradis.* German—*Paradiesnussoel.*
Italian—*Olio di noci del paradiso.*

For tables of constants see p. 638.

This oil is obtained from the seeds of *Lecythis Zabucajo*, Aubl. *Quatelé Zabucajo*, a large tree belonging to the *Myrtaceæ*, and indigenous to Guiana and Brazil. The seeds contain from 50-51 per cent of oil.

The constants given in the table were determined by *De Negri* with an oil obtained from the Sapucaja nuts by extraction with petroleum ether. The oil was slightly yellow, odourless, and had an insipid taste; its acid value was 3·19. The oil was insoluble in cold glacial acetic acid, but dissolved in an equal volume of the hot acid. *De Negri* stated an acetyl value of 44·08 for the specimen examined by him; it is, however, doubtful whether the acetyl value is in this case a constant (due to the presence of a hydroxylated acid) or a variable, notwithstanding the fact that the amount of diglyceride and monoglyceride must have been small.

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[1] De Negri, *Journ. Soc. Chem. Ind.* 1898, 1156.

[TABLE

Physical and Chemical Constants of Paradise Nut Oil

Specific Gravity.		Solidifying Point.		Saponification Value.		Iodine Value.		Refractive Index.	
								Butyro-refractometer.	
At 15° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	At 15° C.	Observer.
0·895	De Negri	4	De Negri	173·6	De Negri	71·64	De Negri	61·3-61·5	De Negri

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.	
° C.	Observer.	° C.	Observer.	Per cent.	Observer.
28·5	De Negri	37·6	De Negri	72·3	De Negri

SECALE OIL[1]

French—*Huile de scigle ergoté.* German—*Mutterkornoel.*
Italian—*Olio di segale cornuta.*

Physical and Chemical Constants of Secale Oil

Specific Gravity at 13° C.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Hehner Value.
0·9254	178·4	71·08	0·20	96·3

Secale oil is obtained from *Secale cornutum.*

Mjöen states that the oil has the acetyl value 62·9. The melting point of the fatty acids was 39·5°-42° C.

Castor Oil Group

In this group I comprise grape seed oil and castor oil. These two oils (pending further confirmation as regards grape seed oil) are remarkable for their high proportion of glycerides of hydroxylated fatty acids as indicated by their high acetyl values. Owing to this composition castor oil is miscible with alcohol. This property is not shared by grape seed oil; for this reason also it is doubtful whether grape seed oil is related to castor oil.

GRAPE SEED OIL

French—*Huile de raisins.* German—*Traubenkernoel.*
Italian—*Olio di vinacciuoli.*

For tables of constants see p. 641.

Grape seed oil is obtained from grape seeds by expression. The freshly expressed grape yields 25 per cent of seeds containing 6-16 per cent of oil. The seeds from white grapes are richer in oil than those from black grapes; sweet grapes yield more oil than those containing little sugar. At the time of vintage the seeds contain the largest amount of oil; on storing the amount of oil decreases to a large extent.

The oil obtained by cold expression has a golden-yellow colour, and is free from odour. Oil from stored seeds is darker and has a

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[1] Mjöen, *Archiv. d. Pharm.* 1894 (234), 278

slightly bitter flavour. Oil of the second expression is brown and has a bitter taste. The numbers recorded in the table refer to extracted oil. The oil dissolves easily in glacial acetic acid at 70 C.; the solution becomes turbid at 66·5° C. In 96 per cent alcohol it dissolves only partially.

Grape seed oil does not dry on exposure to air, or only after a long time (*De Negri* and *Fabris*).

The most prominent characteristic of this oil is, according to *Horn*, its very high **acetyl value**, placing it, in this respect, in close relationship to castor oil. Since this number was obtained by *Benedikt* and *Ulzer's* method, it stands in need of confirmation. The high specific gravity stated by *Horn*, in conjunction with the low saponification value, would seem to confirm the high proportion of hydroxy acids. Yet the specific gravity ascertained by *De Negri* and *Fabris*, and its immiscibility with alcohol, negatives a high proportion of hydroxy acids. The low saponification number found by *De Negri* and *Fabris* (practically identical with that stated by *Horn*) speaks, however, in favour of *Fitz's* statement,[1] that grape seed oil contains largely erucic acid. This was isolated from the ether-soluble lead salts as a solid acid of the melting point 33° C., yielding, on fusion with caustic potash, a considerable amount of arachidic acid. The sample examined by *Horn* had the acid value 16·2. Grape seed oil is expressed in various localities; the cold drawn oil is used as an edible oil, the oil expressed in the hot is used for burning. *Horn*[2] proposed the employment of this oil as a substitute for castor oil in the manufacture of Turkey-red oil.

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[1] *Berichte*, 1871, 442.

[2] *Mitth. des k. k. technolog. Gewerbe-Museums*, 1891, 185.

Physical and Chemical Constants of Grape Seed Oil

Specific Gravity.		Solidifying Point.		Saponific. Value.		Iodine Value.		Reichert-Meissl Value.		Hehner Value.		Maumené Test.		Acetyl Value.	
At 15° C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.		Ob-server.
0·926	Jobst	−11	Jobst	178·4	Horn	94	Horn	0·46	Horn	92·13	Horn	52-54	De Negri and Fabris	144·5[1]	Horn
0·9202	Hollandt	−15 to −17	Hollandt	178·5-179	De Negri and Fabris	95·8-96·2	De Negri and Fabris								
0·9561	Horn	−10 to −13	De Negri and Fabris												
0·935	De Negri[2] and Fabris														

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
20-18	De Negri and Fabris	23-25	De Negri and Fabris	187·4	Horn	98·65	Horn
...	...	...	...	...	...	98·9-99·05	De Negri and Fabris

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[1] This value requires confirmation, having been determined by *Benedikt* and *Ulzer's* method.

[2] *Annali del Labor. chimico centr. delle Gabelle*, 1893, 225.

CASTOR OIL

French—*Huile de ricin.* German—*Ricinusoel.*
Italian—*Olio di ricino.*

For tables of constants see pp. 645-647.

Castor oil is obtained from the seeds of *Ricinus communis.*

The seeds contain from 46 to 53 per cent of oil; they consist of 20 per cent of husks, which are rich in mineral matter but contain no oil, and 80 per cent of kernels forming a white, softish mass.

The most important sources of castor seed are East India, Java,[1] the Mediterranean countries, and the United States of America. On a large scale, about 40 per cent of oil are obtained by expression, 33 per cent being yielded by the first expression and the remainder by the second expression. The oil is also prepared by extraction on a manufacturing scale. The expressed oil, especially the cold drawn oil, is used for medicinal purposes, the toxic principle (the alkaloid "ricin") not passing into the oil. The cake also retains the bulk of the powerful fat-hydrolysing enzyme in the seeds (cp. chap. ii.).

The lower qualities of oil, those of the second and third expression, are employed for manufacturing purposes. The expressed or extracted meal can only be used as manure, although attempts have been made to apply the pressed cake to feeding purposes, after freeing it from the poisonous alkaloid "ricin."[2] Since the pressed cake retains about 8 per cent of oil, it is usually ground to meal and extracted in order to recover the oil before the meal is sold as manure. For the best quality of oil (for medicinal purposes) the seeds are decorticated prior to expression. For this purpose special decorticating machinery is being employed. The seed is passed between rollers set at such a distance that the outer shell only is broken. The kernels are then separated from the light husks by a blast of air, which carries away the husks.

In the usual process of refining the oil by steaming, any castor seed enzyme which may have passed together with any meal into the oil in the process of expression, is destroyed. Hence properly refined castor oil keeps very well, and does not turn easily rancid, as long-extended observations in my laboratory have shown. A sample exposed to the atmosphere for four years contained only 1 per cent of free fatty acids.

Most commercial samples contain, therefore, only very small proportions of free fatty acids, as evidenced by the numbers collated in the following table:—

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[1] *Journ. Soc. Chem. Ind.* 1895, 321.

[2] Cp. O. Nagel, *Journ. Soc. Chem. Ind.* 1902, 30.

[TABLE

Free Fatty Acids in Castor Oil

Description of Oil.	No. of Samples.	Free Fatty Acids, calculated to Oleic Acid.	Observer.
		Per cent.	
Expressed oil	9	0·68-14·61	Nördlinger
Extracted oil	5	1·18-5·25	,,
Commercial oil	2	1·46-2·16	Thomson and Ballantyne
Indian oil	23	0·14-1·06	Deering and Redwood

Castor oil is a colourless or pale greenish oil, having a taste at first mild, then harsh ; this harsh taste is more pronounced in American than in Italian or French oils. The oil is very viscous. Contrary to older statements, it does not dry even when exposed in thin layers. A sample of medicinal oil, which I kept exposed for four years, had the specific gravity increased from 0·9591 to 0·9629 (the iodine value had, however, *not* decreased).

An enquiry into the changes which castor oil undergoes on blowing with air, is being carried out in my laboratory. The results obtained so far (unpublished experiments) are detailed in the following tables :—

Blown Castor Oil (Lewkowitsch)

	Original Oil.	Blown 2 Hours at 150° C.	Blown 4 Hours at 150° C.	Blown 6 Hours at 150° C.	Blown 10 Hours at 150° C.
Colour	very light	light	light	light	orange yellow
Specific gravity at 60° F.	0·9623	0·9663	0·9798	0·9778	0·9906
Acid value	1·1	1·3	2·4	2·6	5·7
Saponification value	179·0	182·3	185·2	184·8	190·6
Iodine value	...	83·5	79·63	78·13	70·01
Acetyl value	146·9	150·7	154·3	159·0	164·8
Saponification value of acetylated oil	303·9 304·3	306·5 306·0	308·3 308·7	308·3	311·0

Blown Castor Oil Fatty Acids (*Lewkowitsch*)

	Original Fatty Acids.	Blown 2 Hours at 150° C.	Blown 4 Hours at 150° C.	Blown 6 Hours at 150° C.	Blown 10 Hours at 150° C.
Colour	clear	yellow	dark	very dark	black
Specific gravity at 60° F. . .	0·9543	0·9507	0·9529	0·9525	0·9561
Acid value	174·7	149·3	128·5	112·2	93·73
Saponification value . . .	176·5	173·7	177·5	177·3	181·1
Iodine value	...	86·51	86·77	85·14	85·23
Acetyl value, after removal of some solid fatty acids[1] (dihydroxystearic)	133·1	94·26	105·5	93·31	81·4
Saponification value of acetylated acids	299·2	284·4	272·6	272·3	264·9

As *Peter* has shown first, castor oil is strongly dextro-rotatory. This is confirmed by *Deering* and *Redwood*, who observed a strongly marked rotatory power in the twenty-three samples of Indian castor oil they examined, the rotation caused by 200 mm. of oil varying from + 7·6° to + 9·7° in a *Hoffmann-Laurent* polarimeter. The optical activity is no doubt due to presence of an asymmetric carbon atom in ricinoleic acid.

If castor oil is allowed to stand in the cold, 3 to 4 per cent of a solid mass is deposited, consisting, according to *Krafft*,[2] of tristearin and triricinolein, palmitin being absent. Amongst the solid fatty acids *Juillard* discovered dihydroxystearic acid (the first natural hydroxy fatty acid) to the extent of 1 per cent. The chief constituent of castor oil is triricinolein. Triricinolein is, according to *Krafft*, solid in its pure state; and the liquid state of castor oil must be ascribed to a state of superfusion of the oil. *Hazura* and *Grüssner*, however, have shown that the liquid fatty acids from castor oil consist of two isomerides, ricinoleic and isoricinoleic acids; *Krafft's* solid acid is, perhaps, identical with one of these acids (cp. also p. 117, *Mangold*). Olein does not occur in castor oil.[3] Castor oil may therefore be said to consist of a small quantity of tristearin, of the glyceride of dihydroxystearic acid, and the glyceride of ricinoleic acid, all the isomerides being comprised under that term. The proportion of triricinolein calculated from the acetyl value of castor oil, 150, would be $\frac{(3\times 298+38)\times 15}{168\cdot 3}=83\cdot 1$ per cent. Since dihydroxystearic acid—present to an extent of 1 per cent amongst the fatty acids—has the acetyl value 281·9, the percentage of ricinolein can be only about 82. The iodine value of triricinolein being 81·76, 82 per cent of triricinolein would absorb 67 per cent of iodine. Castor oil must therefore contain less saturated fatty acids than ricinoleic. This is indeed borne out by the iodine value of the liquid fatty acids having been found = 106·9.

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[1] The acetyl value of the removed solid fatty acids was 143·3 (theory for dihydroxystearic acid 280·5). From these acids there was obtained a petroleum ether insoluble acid of the melting point 130° C. (melting point of dihydroxystearic acid 131° C.).

[2] *Berichte*, 1888, 2730.

[3] Hazura and Grüssner, *Journ. Soc. Chem. Ind.* 1888, 681.

Physical and Chemical Constants of Castor Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.	
At ° C.		Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. 1/10 norm. KOH.	Observer.
15·5	0·960-0·966	Allen	− 10 to − 12[2]	Schaedler	181	Dieterich	84·4	Hübl	1·1	Lewkowitsch
,,	0·9591[6]	Lewkowitsch			180-183	Itallie	84-84·5	Dieterich		
,,	0·9653-0·9679	Thomson and Ballantyne			178·6-180·2	Thomson and Ballantyne	83·6-83·9	Thomson and Ballantyne		
,,	0·9637-0·9642	Deering and Redwood[1]			176·7-179·1	Deering and Redwood[1]	83·8-85·9	Itallie		
18	0·9602	Long			185·9-186·6	Henriques[3]	83·7-85·3[4]	Deering and Redwood[1]		
20	0·9589	,,			183·3[5]	Lewkowitsch	81·4[5]-90·6[6]	Lewkowitsch		
,,	0·963-0·965	Itallie					86·2-87·1	Wijs		
23	0·964	Dieterich								
25	0·9555	Long								
30	0·9522	,,								
35	0·9488	,,								
94	0·9081	Saussure								
99	0·9096	Allen								
(water of 15·5 = 1)										

[1] Twenty-three samples of Indian oil, *Journ. Soc. Chem. Ind.* 1894, 959.
[2] American oil, which is richer in solid glycerides than Indian or Italian oils.
[3] Java oil.
[4] Calculated from bromine values, 52·8-53·7.
[5] Calcutta oil, second pressing.
[6] Medicinal oil.

Physical and Chemical Constants of Castor Oil—continued

<table>
<tr><th colspan="2" rowspan="2">Acetyl Value.</th><th colspan="4">Thermal Tests.</th><th colspan="3" rowspan="2">Refractive Index.</th><th colspan="2" rowspan="2">Viscosity in Redwood's Viscosimeter.</th></tr>
<tr><th colspan="2">Maumené Test.</th><th colspan="2">Heat of Bromination.</th></tr>
<tr><th></th><th>Observer.</th><th>° C.</th><th>Observer.</th><th>° C.</th><th>Observer.</th><th>At ° C.</th><th></th><th>Observer.</th><th>Seconds at 100° F.</th><th>Observer.</th></tr>
<tr><td>149·9</td><td>Lewkowitsch</td><td>47</td><td>Maumené</td><td>15</td><td>Hehner and Mitchell</td><td>15</td><td>1·4795-1·4803</td><td>Strohmer</td><td>1160-1190</td><td>Deering and Redwood</td></tr>
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<tr><td></td><td></td><td></td><td></td><td></td><td></td><td colspan="3">Oleo-refractometer.</td><td></td><td></td></tr>
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<tr><td></td><td></td><td>89-92</td><td>Thomson and Ballantyne</td><td></td><td></td><td colspan="2">+43 to +46[1]</td><td>Jean</td><td></td><td></td></tr>
<tr><td></td><td></td><td></td><td></td><td></td><td></td><td colspan="2">+ 37</td><td>Bruyn and van Leent</td><td></td><td></td></tr>
<tr><td></td><td></td><td></td><td></td><td></td><td></td><td colspan="2">+ 40</td><td>,, ,,</td><td></td><td></td></tr>
<tr><td></td><td></td><td></td><td></td><td></td><td></td><td colspan="2">+41 to +42·5</td><td>Deering and Redwood</td><td></td><td></td></tr>
<tr><td></td><td></td><td></td><td></td><td></td><td></td><td colspan="2">+39 to +42</td><td>Pearmain</td><td></td><td></td></tr>
<tr><td></td><td></td><td></td><td></td><td></td><td></td><td colspan="3">Butyro-refractometer</td><td></td><td></td></tr>
<tr><td></td><td></td><td></td><td></td><td></td><td></td><td>At ° C.</td><td>"Degrees."</td><td>Observer.</td><td></td><td></td></tr>
<tr><td></td><td></td><td></td><td></td><td></td><td></td><td>25</td><td>78</td><td>White</td><td></td><td></td></tr>
<tr><td></td><td></td><td></td><td></td><td></td><td></td><td>40</td><td>65·5</td><td>,,</td><td></td><td></td></tr>
</table>

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[1] Java oil.

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.			Solidifying Point.		Melting Point.		Mean Molecular Weight.		Iodine Value.		Refractive Index.	
At ° C.		Observer.	° C.	Observer.	° C.	Observer.		Observer.	Per cent.	Observer.	At 60° C.	Observer.
15·5	0·9509	Allen	3	Hübl	13	Hübl	290-295	Alder Wright	86·6-88·3	Morawski and Demski	1·4546	Thoerner
98-99	0·8960	,,					306·6	Allen	87-88	Thoerner		
							292	Williams				
									Liquid Fatty Acids.			
									106·9[1]	Tortelli and Ruggeri		

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[1] Italian oil, 1898 crop ; iodine value of oil, 87·4.

The amount of unsaponifiable matter in the samples examined by *Thomson* and *Ballantyne* varied from 0·30 to 0·37 per cent.

The specific gravity of castor oil, its behaviour with solvents, its acetyl value, and its very high viscosity afford ready means of identification.

Castor oil has the highest **specific gravity** of any natural fatty oil; only the "blown oils" (chap. xv.) acquire so high a gravity in the course of manufacture. Hence the presence of a foreign fatty oil in castor oil would in the first instance be recognised by a lower gravity of the sample than 0·960. Rosin oil of specific gravity 0·998, which may have been added to an adulterated oil in order to mask the influence of a foreign fatty oil, can be easily detected by determining the unsaponifiable matter.

Of all known oils castor oil has the highest **viscosity**, only "blown oils" (chap. xv.) and rosin oil approaching it in this respect. The viscosity of the twenty-three samples examined by *Deering* and *Redwood* was from 1160 to 1190 seconds for 50 c.c. at 100° F.

Castor oil is miscible in every proportion with glacial acetic acid and **absolute alcohol**. It also dissolves, at 15° C., in 2 volumes of 90 per cent, and in 4 volumes of 84 per cent alcohol. *Italie*[1] has determined the solubility of five samples of castor oil (three of which, A, B, C, had been expressed in the laboratory at the temperatures of 20° C., 50° C., and 80° C. respectively, whereas D and E were commercial oils) in 90 per cent alcohol, with the following result:—

10 c.c. of Oil.	Require 90 per cent Alcohol at 20° C. c.c.
A	26·4
B	26·8
C	27·8
D	29·4
E	24·0

For the rapid examination of castor oil (as by custom-house officers), *Finkener*[2] recommends agitation of 10 c.c. of the sample with 50 c.c. of alcohol, specific gravity 0·829 at 17·5° C., in a graduated cylinder. A strong turbidity, which does not disappear even at 20° C., shows that the oil is not pure; even 10 per cent of foreign oils (as sesamé, linseed, rape, cotton seed oils) may thus be detected.

Castor oil is nearly insoluble in **petroleum ether**, kerosene, and paraffin oils. At a temperature of 16° C. as little as 0·5 per cent of castor oil in these solvents causes a turbidity. However, castor oil gives a homogeneous solution with an *equal* measure of petroleum ether, or a volume and a half of kerosene or paraffin oil; if more of the solvents is used, any excess will float on the top of the mixture. The characteristic insolubility is lost at the ordinary temperature if castor oil be adulterated with a small quantity of a soluble oil.

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[1] *Chem. Zeit.* 1890, Rep. 367.

[2] *Journ. Soc. Chem. Ind.* 1887, 148.

Castor oil is distinguished from all other oils—with the exception only of grape seed oil (pending further examination of grape seed oil) by its very high **acetyl value**. The determination of this constant furnishes, therefore, the surest means of ascertaining its purity, and enables the analyst to estimate the amount of adulteration.

Also the **saponification value** (approaching that of the oils belonging to the rape oil group) and the **iodine value** will afford means of detecting fraudulently added oils.[1]

In the **elaïdin test** castor oil gives a whitish solid mass, due to the formation of ricinelaïdin.

The price of castor oil is at present so low that adulteration with a fatty oil will hardly be practised. Still, at times when castor oil was much higher in price, adulteration with rape oil, rosin oil, and chiefly with blown oils, did occur.

Rosin oil will be easily detected by determining the unsaponifiable matter.

The "**blown oils**," although simulating castor oil in specific gravity and viscosity, differ from it in having much lower acetyl values, higher saponification values (see chap. xv.), and lesser solubilities in alcohol.

Castor oil is easily detected in other oils by the high acetyl value and the high specific gravity of the oil.

On nitrating castor oil with concentrated nitric and sulphuric acids, "nitrated" castor oil is obtained (cp. chap. xv.).

Castor oil is used in medicine (the purgative action of the oil being due to ricinoleic acid), in soap-making, and in the manufacture of Turkey-red oils. In India it is largely used as a lubricant for locomotive bearings, but in this country it is too thick to be serviceable for this purpose. Castor oil is, however, largely used as a lubricant for leather-belting in heavy work.

On a smaller scale castor oil is subjected to destructive distillation for the preparation of "cognac oil," when undecylenic acid and œnanthaldehyde pass over, whilst the remaining mass solidifies to a very bulky, spongy, india-rubber-like mass, for which a solvent has not yet been found.[2]

The residue, after successive washings with alcohol, chloroform, and ether, was found to have the composition[3] $C_{33}H_{58}O_5$, corresponding to the anhydride of triundecenoic (triundecylenic) acid, $(C_{11}H_{20}O_2)_3 - H_2O$. On melting the product with potassium hydroxide, it yields hexadecenoic acid (hexaundecylenic acid), $C_{16}H_{30}O_2$. On oxidising with fuming nitric acid, sebacic acid and an acid of the formula $C_{13}H_{22}O_4$ were obtained; by oxidation with potassium permanganate, sebacic acid and lower fatty acids were produced. If the distillation of castor oil be stopped just before the mass would become converted to the india-rubber-like substance, the oily residue still contains glycerides;

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[1] The saponification and iodine values given by Thoerner, viz. 201-203 and 93-94 respectively are so abnormal that they have been omitted from the table of constants.

[2] *Berichte*, 1876, 2034.

[3] Fendler and Thoms, *Archiv d. Pharm.* 1901 (239), 1.

this residue corresponds to the composition $C_{105}H_{148}O_{18}$, which appears to be the glyceride of the dibasic triundecenoic (triundecylenic) acid :—$(C_3H_5)_2(C_{33}H_{58}O_6)_3$ (cp. chap. xv. "Polymerised Oils").

Lesser Known Non-drying Oils

Oil from	Source.	Native Country.	Yield. Per cent.	Saponification Value.	Iodine Value.	Solidifying Point of Fatty Acids. °C	Observer.
Loue-Moue seed	...	Assam	...	...	87·0	12·5	Miliau[1]
Birch seed .	Betula alba	Europe	...	211·0	83·6	...	Lidoff[2]
	Lecythis urnigera Mart.	Brazil	...	198·57	83·1	...	Niederstadt[3]
	Camellia Drupifera	Cochin China	28-35	...	68·0	...	Pottier[4]
	Cyperus esculentus, L.	Brazil	...	224·72	62·3	...	Niederstadt
	Anacardium occidentale, L.	,,	...	179·84	60·6	...	,,
Coula . .	...	Gaboon	5·5	...	...	...	Lecomte and Hébert[5]
Kô-sam seed[6] .	Brucea sumatrana	Indian Archipelago	20	...	...	...	Power and Lees
Spice bush seed (Fever bush seed)	Lindera Benzoin	United States	45·6	284·4	...	...	Caspari[7]

2. ANIMAL OILS

In this section I describe the oils obtained from animals, under the following two classes—

(1) Marine animal oils,
(2) Terrestrial animal oils.

This subdivision is not made merely for the sake of convenience; it is based on striking chemical differences. Broadly speaking, these two groups may be compared with the two large classes of vegetable oils :—the drying and the non-drying oils.

[1] *Journ. Soc. Chem. Ind.* 1900, 54.

[2] *Zeit. f. ang. Chem.* 1899, 132.

[3] *Berichte d. deutsch. pharm. Gesell.* 1902, 144.

[4] The sample is stated to have the specific gravity 0·980, and to rotate the plane of polarised light in a 200 mm. tube 1·8° to the right (*Les nouveaux remèdes*, 1900, 16, 121).

[5] *Journ. Soc. Chem. Ind.* 1895, 493.

[6] The oil consists chiefly of the glycerides of stearic, palmitic, oleic, and linolic acids; the oil also contains a hydrocarbon of the formula $C_{31}H_{64}$, melting at 67°-68° C.

[7] *Amer. Chem. Journ.* 1902, 291.—Melting point of oil, 26° C.; Reichert value, 1·29-1·34. The oil is stated to consist of the glycerides of capric, lauric, and oleic acids, laurin preponderating.

Like the drying oils the marine animal oils are characterised by very high iodine values, by the large amount of hexabromides they yield, by their somewhat power of absorbing oxygen, and by not yielding elaïdins.

The terrestrial animal oils resemble the non-drying oils in that they have low iodine values, do not easily absorb oxygen, and yield solid elaïdins.

Just as amongst the vegetable oils there are a number of oils occupying an intermediate position between the drying and the non-drying oils, viz. the semi-drying oils, we find among the marine animal oils gradations from the most pronounced type of easily oxidisable oils to oils containing large quantities of glycerides of saturated fatty acids, thus approaching the chemical constitution of terrestrial animal oils.

(1) MARINE ANIMAL OILS

The members of this class may be conveniently subdivided into the following three groups :—

α. Fish oils.
β. Liver oils.
γ. Blubber oils.

The term "train oil" has been avoided, as its German equivalent "Trane" includes all three groups, and is therefore apt to cause confusion. It must further be premised that, under blubber oils, those oils only are included that consist wholly or in greater part of glycerides. Therefore the liquid waxes—viz. sperm oil and Arctic sperm oil, which are frequently classed together with blubber oils—are excluded from this group, since, according to their chemical constitution, they belong to the waxes proper.

The oils belonging to this class are liquid at the ordinary temperature, yielding, however, on cooling, varying amounts of solid glycerides. They are readily distinguishable from other liquid fats by their fishy taste and smell.

The specific gravities of the marine animal oils vary between 0·901 and 0·930. The saponification values of some of the blubber oils deviate widely in both directions from the mean value of the vegetable oils—195—according as they contain large amounts of spermaceti or of glycerides of volatile fatty acids. Hence this constant cannot be used as a basis for subdivision.

The liver oils, however, appear to form a natural group, characterised by notable amounts of cholesterol and other biliary substances. Since, for the purposes of subdivision, I adopt the iodine value as the basis, the liver oils may be interposed between the fish oils and the blubber oils.

The earlier statements that the marine animal oils are characterised, and can be differentiated from all other fatty oils by the intense colouration they give with caustic soda, sulphuric acid, nitric acid, and phosphoric acid, must be considered as valueless.

Phosphoric acid, in particular, was proposed as a very characteristic reagent, capable of detecting even 0·1 per cent. of these oils in vegetable oils. The best results were stated to be obtained by warming five measures of the oil under examination with one volume of syrupy phosphoric acid, when all oils belonging to this class, both in their pure state or in admixture with other oils, were said to show intensely red, reddish-brown, or brownish-black colourations. *Holde*[1] stated that the phosphoric acid test was uncertain, as on the one hand rosin oils produce red colourations with this acid, and on the other hand distinct colourations only appear when large quantities of marine animal oils are present in other oils. The writer,[2] after an exhaustive examination of these colour reactions, has come to the conclusion that they are by no means characteristic of these oils, but are due to impurities which can be removed by proper modes of refining. Thus, a sample of horses' foot oil (not refined), prepared in the laboratory, gave, with the above-mentioned reagents, colourations which might be considered as typical of marine animal oils. Also *old* samples of linseed and cotton seed oils behaved similarly.

The same conclusion holds good of the chlorine test.

Owing to the large amount of unsaturated fatty acids which the oils belonging to this class contain, they develop a considerable amount of heat in the thermal tests. They also absorb notable amounts of oxygen without, however, drying to a flexible skin like the best drying vegetable oils.

The nature of the fatty acids in these oils is very imperfectly known. Some of them have high *Reichert* values, pointing to the presence of large quantities of volatile acids. Others deposit "stearine" on cooling, which appears to consist chiefly of palmitin. Most of these oils consist of glycerides of unsaturated fatty acids, as is shown by their high iodine values, ranging from 120 upwards. These high iodine values, especially those of the fish and liver oils, clearly point to the presence of acids less saturated than such as belong to the oleic series. It is by no means certain that oleic acid occurs in these oils. The physetoleic acid of the earlier authors could not be detected by *Fahrion*.[3] *Bull's*[4] statement that all oils belonging to this class—with the exception of cod liver oil—contain erucic acid, as also an acid of the formula $C_{20}H_{38}O_2$, requires confirmation. The less saturated acids cannot be identical with linolic or linolenic acids, as the oils, although absorbing large amounts of oxygen, do not dry like linseed oil.[5] In the hexabromide test the marine animal oils yield considerable amounts of brominated glycerides. These differ, however, from the hexabromides obtained from vegetable drying oils, for the bromides prepared from the

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[1] *Journ. Soc. Chem. Ind.* 1890, 419.

[2] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1894, 617. Cp. chap. vii. p. 329.

[3] *Journ. Soc. Chem. Ind.* 1893, 938; 935.

[4] *Chem. Ztg.* 1899, 996.

[5] The free fatty acids from seal and cod liver oils kept in stoppered glass bottles deposit, after a few months' standing, a resinous substance. (Lewkowitsch.)

mixed fatty acids (in the same manner as the linolenic hexabromide is obtained), do not melt, like linolenic hexabromide, at about 175° C., but remain solid up to even 200° C., when the mass becomes black, without, however, melting to a liquid.

Fahrion[1] is of the opinion that he has proved the presence of an unsaturated acid, $C_{18}H_{30}O_2$—jecoric acid—(cp. p. 115), and infers the presence of an unsaturated acid of the composition $C_{17}H_{32}O_2$—asellic acid—from a dihydroxylated acid (dihydroxyasellic acid) obtained on oxidising the fatty acids of sardine oil. *Heyerdahl* claims to have discovered two unsaturated acids in cod liver oil, viz. jecoleic acid (p. 110) and therapic acid (p. 116). Finally *Bull* assumes amongst the liquid fatty acids of cod liver oil an acid of the composition $C_{23}H_{36}O_2$, belonging to the series $C_nH_{2n-10}O_2$. The existence of all the last mentioned acids is so far hypothetical. An investigation of this subject is therefore still a desideratum.

Halphen[2] recommends as a general test for the presence of marine animal oils, a reagent consisting of 28 volumes of glacial acetic acid, 4 volumes of nitrobenzene, and 1 volume of bromine. This reagent differs from the one employed in the hexabromide test merely by the presence of nitrobenzene. Evidently this test does not therefore admit of a differentiation of the marine animal oils from the vegetable drying oils. The same stricture holds good for the further suggestion made by *Halphen* to differentiate the hexabromides obtained from linseed oil on the one hand, and from fish oils on the other, by the behaviour with boiling carbon tetrachloride. As experiments made in my laboratory have proved, the linseed oil hexabromide does dissolve in carbon tetrachloride, and gives a somewhat crystalline precipitate on cooling, whereas fish oil hexabromide does not dissolve completely and gives a gelatinous precipitate on cooling. It would, however, be impossible to thus differentiate linseed oil from fish oils; more hopeless still is it to detect thereby fish oil in linseed oil. The differences in the melting points of the hexabromides of the mixed fatty acids are so characteristic that we can dispense with the *Halphen* solubility test.

a. Fish Oils

The fish oils are obtained from all parts of the body of common fish—such as herring, sardine, salmon, sprat, etc.—by boiling. The livers of these fish contain, as a rule, very little oil, whereas the bodies of the liver-oil yielding fish, notably cod fish, yield so little oil, that it is not prepared commercially.

It should be noted that the industry of fish oils has undergone a very important change during the last decade, in consequence of the replacement of fishermen's sailing boats by steamers. Whereas in former times fishing boats would remain out at sea for about a week or two, the fish are at present brought to shore (*i.e.* into the

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[1] *Journ. Soc. Chem. Ind.* 1893, 938; 935.

[2] *Journ. Pharm. Chim.* 1894, 259, 391.

rendering establishment) almost within one day. Thus the deteriorating changes, due to the oil having remained in contact with highly putrescible matter for some time, has been obviated to a large extent. The very dark colour and rank odour which used to characterise fish oils has therefore given place to a somewhat paler colour and a much less unpleasant, though strongly pronounced, fishy smell. Oils so obtained lend themselves readily to refining operations, although special processes applied to oils of rank odour have brought also these within the reach of industrial application.

It should further be noted that in consequence of these improvements, as also in consequence of the erection of establishments in which rendering is carried on on a large scale, the separation of cod livers from the bodies of oil yielding fish is performed more carefully, so that commercial fish oils are now comparatively free from liver oils, which were so prevalent in the fish oils in former years. The analytical numbers published by earlier observers frequently referred to a mixture of fish and liver oils, a fact which found its readiest expression in the large amount of unsaponifiable matter stated to have been found in fish oils. These unsaponifiable matters were due to the presence of liver oils, as also to liquid and solid waxes intermixed with the fish oils.

MENHADEN OIL

French—*Huile de Menhaden.* German—*Menhadenöl.*
Italian—*Olio di Menhaden.*

For table of constants see p. 655.

Menhaden oil is an American fish oil, and, like other fish oils, is prepared from the body of fish, especially of the menhaden, *Alosa Menhaden* (*Brevoortia tyrannus*), a fish somewhat larger than a herring. From about May until November this fish appears in enormous quantities off the Atlantic coast (especially of New Jersey), so that as much as 400,000 tons are caught in one season. The fish is delivered from the steamers straight into large boiling pans. The resulting oil is brought into commerce under the following names according to the quality:—prime crude; brown strained; light strained, bleached winter oil; bleached winter white. The last two brands are oils freed from "stearine." The residue left in the boiling pans is sold as manure ("fish scrap").

Menhaden oil consists almost entirely of glycerides, as shown by its saponification value, the proportion of glycerol it yields on saponification and the small amount of "unsaponifiable matter." The chemical composition of the unsaturated glycerides is not known yet. *Bull* states that he isolated from a specimen of Menhaden oil 2·3 per cent of a fatty acid, having the neutralisation value 197·0, and absorbing 312·5 per cent of iodine.

Physical and Chemical Constants of Menhaden Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Reichert Value.		Iodine Value.		Maumené Test.	
°C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.
15	0·9311	Bull	−4	Jean	192	Allen	1·2	Allen	147·9	Archbutt	126	Allen
15·5	0·927-0·933	Allen	...	...	189·3	Thomson and Ballantyne	...	...	160	Thomson and Ballantyne	123-128	Archbutt
,,	0·9311	Thomson and Ballantyne			188·7	Bull			153·9	Schweitzer and Lungwitz		
					193[1]	,,			172·6	Bull	Specific Temp. Reaction.	
									139·2[1]	,,	306	Thomson and Ballantyne

[1] "Natural pressed" menhaden oil.

Unsaponifiable Matter

Colour of the Oil.	Per cent.	Observer.
Pale yellow . .	0·61	Fahrion
Red . . .	0·82	,,
Yellowish-red (Levantine)	1·43	,,
Brown	1·60	Thomson and Ballantyne
Extra pale . . .	1·43	Bull

Jean states that menhaden oil usually contains 0·02 per cent of iodine.

Menhaden oil is frequently adulterated with mineral oil and rosin oils.

Its principal use is in the currying trade, and in the manufacture of sod oil. The oil is also employed for adulterating Newfoundland cod liver oil and paint oils.[1]

SARDINE OIL, JAPAN FISH OIL

French—*Huile de Sardine, Huile du Japon.* German—*Sardinenöl, Japanisches Fischoel.* Italian—*Olio di Sardine, Olio di Sardine del Giappone.*

For table of constants see p. 657.

This oil is obtained in the preparation of tinned sardines.

The Japanese sardine oil—Japan fish oil—prepared on a large scale in Japan, is extracted from *Clupea sardinus.* The fish is chopped and the oil obtained by boiling with water, followed by pressing. When there is a scarcity of labour—as happens during the fishing seasons—the fish is allowed to rot in heaps, when the greater part of the oil flows out, the remainder being subsequently recovered by pressure. The oil obtained by the first process is limpid and can be easily refined, whereas the oil from the second process has a very dark colour and a nauseous taste. The crude oil contains about 30 per cent of "stearine."[2] It is refined in Yesso and Yokohama by heating to 50°-60° C. for an hour, and then run off into wooden vessels, where it separates into three layers. The upper layer is liquid and clear, the middle layer consists of solid fat,[2] and the lowest of water intermixed with albuminous substances and portions of the fish.[3] Some constants of this oil, which seem to differ from ordinary sardine oil, especially in its iodine absorption, have been recorded in the table of constants given, p. 657.

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[1] E. W. Mann, *Journ. Soc. Chem. Ind.* 1903, 1357, describes a menhaden oil containing 6·73 per cent of unsaponifiable matter, and having the Reichert value 2·2 and the iodine value 145·8. These abnormal numbers have not been embodied in the tables.

[2] This solid fat, brought into commerce under the name "refined fish tallow," is chiefly used as a dégras substitute for currying leather (*Journ. Soc. Chem. Ind.* 1894, 894).

[3] Villon, *Les Corps gras*, 1887, 178; *Journ. Soc. Chem. Ind.* 1887, 372.

Physical and Chemical Constants of Sardine Oil

	Specific Gravity.		Melting Point.		Saponification Value.		Iodine Value.		Hehner Value.		Refractive Index.	
											Oleo-refractometer.	
	15° C.	Observer.	Per cent.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	Per cent.	Observer.	"Degrees."	Observer.
Sardine oil .	0·933	Fahrion					193·2	Fahrion	94·5	Fahrion	+50 to +53 at 45 °C	Jean
Japan fish oil .	0·916	,,	20-22	Villon	189·8-192·1	Lewkowitsch	121·5	Lewkowitsch	95·93	,,		
	0·9272-0·9338	Bull			189-193·7	Bull	100-164 134·1-171·3	Fahrion Bull				

Physical and Chemical Constants of the Mixed Fatty Acids

	Solidifying Point. Titer Test.	
	°C.	Observer.
Japan fish oil .	27·6-28·2	Lewkowitsch

Some further numbers are given in the following table, due to *Fahrion* :—

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
	Iodine Value.	Acid Value.	Hehner Value.	Oxidised Acids. Per cent.	Unsaponifiable. Per cent.	Fatty Acids freed from Oxidised Acids. Per cent.	Molecular Weight of VI.	Neutralisation Value of the Fatty Acids freed from Oxidised Acids.[1]
Japan fish oil, pale . .	164·0	10·8	95·52	1·16	0·52	93·84	282·8	185·8
,, brown . .	157·6	34·2	96·58	0·75	0·67	95·16	281·7	189·1
,, pale . .	135·7	12·3	97·04	0·41	0·82	95·81	295·7	181·4
,, reddish-brown	108·5	34·5	96·82	0·62	0·86	95·34	296·6	180·0
,, yellow . .	100·1	28·2	96·51	0·49	0·79	95·23	290·2	183·8
Sardine oil, yellow . .	191·7	19·2	95·60	0·61	0·48	94·51	285·7	185·2
,, red . . .	167·9	21·7	96·55	1·35	1·01	94·19	297·7	177·2
,, reddish yellow	160·9	4·6	97·08	0·94	0·63	95·51	299·5	179·5

The solid fatty acids in a specimen of sardine oil examined by *Fahrion* were at first stated to consist of palmitic acid only; afterwards he modified this statement by allowing a small quantity of stearic acid, palmitic, however, preponderating. The liquid fatty acids did not contain physetoleic acid (p. 101), nor could oleic, linolic, or either of the two linolenic acids be detected. The unsaturated fatty acid was stated to be *jecoric acid*, $C_{18}H_{30}O_2$ (from *jecur*, liver; though sardine oil is not a liver oil), an isomeride of linolenic acid, but differing from it essentially in that it does not conform to *Hazura's* rule (p. 360). According to this rule it should yield, on oxidation with potassium permanganate in alkaline solution, a hexahydroxy acid, whereas it is apparently broken down with formation of carbonic and volatile fatty acids. *Fahrion*, therefore, considered this specimen of sardine oil to consist of

Tripalmitin, 14·3 per cent.
Trijecorin, 85·7 ,, ,,

These results have been severely criticised by *Weiss*,[2] and stand therefore in need of confirmation.

A sample of Japan fish oil examined in my laboratory by *Walker* and *Warburton*[3] yielded 21-22 per cent of hexabrominated glycerides; the mixed fatty acids gave 23-23·3 per cent of a hexabromide which became black at 200° C. without melting. Another sample of Japan fish oil containing some liver oil, and deodorised by a special process, yielded, in the hexabromide test, 49-53·3 per cent of brominated glycerides; its mixed fatty acids gave 38-39·3 per cent of a brominated product which turned black at 200 C. without melting.

Bull states that he has isolated from a number of Japan fish oils 5·75-26·4 per cent of liquid fatty acids, absorbing 292·8-358·3 per cent of iodine.

Japan fish oil must not be confounded with Japan cod liver oil.

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[1] This value is termed by Fahrion "Inner Saponification Value."

[2] *Journ. Soc. Chem. Ind.* 1893, 937.

[3] *Analyst*, 1902, 237.

LESSER KNOWN FISH OILS

	German.	French.	Italian.	Source.	Specific Gravity.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Oxidised Acids.	Hehner Value.	Mean Molecular Weight of the Mixed Fatty Acids.	Solidifying Point of Fatty Acids.	Melting Point of Fatty Acids.	Butyro-refractometer at 25° C.	Acetyl Value.	Acid Value.	Unsaponifiable.	Observer.
Stickleback .	Stichlingstran .	Huile de trois-épines	Olio di spinello .	Gasterosterus trachurus .	...	...	162·0	...	Per cent. 0·62	95·78	287·4	°C. ...	...	...	...	21·6	Per cent. 1·73	Fahrion
Herring .	Heringsoel . (Heringstran) .	Huile d'hareng .	Olio di aringhe .	Clupea hareugus . .	0·9202-0·9391 (at 15° C.)	179-193·7	131·0-142	...	...	...	...	...	...	...	...	1·8-40·2	1·3-10·7	Bull[1]
,, . .	...	...	...	...	...	...	123·5	...	1·59	95·64	291·9	...	...	...	...	44·6	0·99	Fahrion
Brusmer .	...	...	...	Brosmius brosme . .	0·9222	180·4	130·1	...	...	...	...	...	...	...	...	0·3	4·92	Mann
White fish .	Weissfischoel .	Huile de cyprin .	Olio di argentina .	...	0·9268	201·6	127·4	...	...	...	...	...	...	Refractive Index 1·4795 at 22° C. Butyro-refractometer 76·5 at 25° C.		3·98	...	Bull
Sturgeon .	Störtran . .	Huile d'esturgeon .	Olio di storione .	Accipenser sturio . .	0·9236 (at 15° C.)	186·3	125·3	...	...	...	...	...	...	...	...	0·23	1·78	Bull
Sprat . .	Sprottenoel . (Sprottentran) .	Huile d'esprot .	Olio di sardella .	Clupea sprattus . .	0·9274 (at 15° C.)	194·5	122·5-142	2·4	...	95·1	280	25·4 (?)	27·9	...	8·6	...	1·36	Henseval
Hoi[2] . .	...	...	...	...	0·9186	164·7	116·60	...	...	...	...	...	...	...	...	...	15·06	Mann
Carp . .	Karpfenoel . .	Huile de carpe .	Olio di carpione .	Cyprinus carpio . .	0·9107 (at 27·2° C.)	202·3	84·3	2·1	...	...	277·7	28	33·4	...	12·9	0·18	...	Zdarek[3]
Cramp fish .	...	...	...	...	0·909	148·2 (?)	107·3	...	...	...	...	...	...	...	...	0·79	21·97	Bull
Sun fish .	...	...	...	...	0·901	147·6 (?)	102·7	...	...	...	...	...	...	...	...	2·15	24·12	,,

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[1] Seven samples containing 10-13·3 per cent of liquid acids having iodine values from 289·3-319·8.

[2] Norwegian name.

[3] *Zeit. physiolog. Chem.* 1903, 460.

SALMON OIL

French—*Huile de Saumon.* German—*Lachsoel.*
Italian—*Olio di Salmone.*

This oil is obtained on a very large scale from the salmon (*Salmo salar*) as a by-product in the salmon tinning industry of British Columbia. The oil is pale golden yellow, has a mild smell, and tolerably pleasant taste.

The sample examined in my laboratory by *de Greiff*[1] gave the numbers recorded in the table of constants.

Physical and Chemical Constants of Salmon Oil

Specific Gravity at 15·5° C.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Hehner Value.
0·92586	182·8	161·42	0·55	95·02

Iodine Value of the Liquid Fatty Acids

197·4

The oil is imported in large quantities into this country.

Lesser known fish oils, see table opposite.

β. Liver Oils

The liver oils contain notable amounts of cholesterol and other unsaponifiable substances. These bodies must be looked upon as the chromogenetic substances producing the colour reactions (especially when the oils are rancid) which were formerly considered as characteristic of liver oils. At present only the sulphuric acid colour test can be looked upon as having decisive importance; the blue colouration which pure and fresh liver oils give in a solution of carbon bisulphide with conc. sulphuric acid is very distinct; if the oils are rancid a purple colouration takes the place of the blue. Experiments carried out in my laboratory on a number of liver oils obtained from different fish, as also experiments by *Tichomirow* and *Kaiser*,[2] confirm that this colour reaction is a general one for liver oils.

The intensity of the phospho-molybdic acid test (cp. p. 330) is also characteristic. If the chloroformic solution of a liver oil, after shaking with the phospho-molybdic acid reagent, be allowed to stand,

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[1] *Chem. Revue*, 1903, 223.

[2] *Chem. Zeit.* 1895, Rep. 310.

there is formed a blue ring at the zone of contact of the two layers, no doubt due to the neutralising action of the bases in the oil. In this form the phospho-molybdic test may serve to identify a liver oil. Rancid liver oils, however, do not give a distinct colour reaction.

COD LIVER OIL

French—*Huile de foie de morue.* German—*Dorschleberoel, Leberoel.*
Italian—*Olio di fegato di merluzzo.*

For tables of constants see pp. 661, 662.

Genuine cod liver oil is obtained from the liver of the cod, *Gadus morrhua* (and the dorsch, the young of *G. morrhua*, formerly considered as a separate species, *Gadus callarias*).

The following three qualities of cod liver oil, as obtained by the natural decay of the livers (in the Lofoten islands), are known in commerce: (1) pale cod liver oil, (2) light brown oil, (3) brown oil.

Pale cod liver oil[1] and *light brown oil* are used in pharmacy. The former is the first product, the light brown oil forming the second product, after the disintegration of the livers has proceeded further. At present large quantities of medicinal oil are prepared by heating the livers in jacketted vessels by steaming, when the cell membranes burst and the oil exudes—"steam liver oil." The medicinal cod liver oil prepared in this country is exclusively obtained by the steam process. The livers must be absolutely fresh; they are taken from fish brought ashore alive and "steamed" the same day.

The *brown oil*—the "cod oil" of commerce—is also a genuine cod liver oil. If the fish cannot be brought alive to shore, they are opened in the fishing boat and the livers collected. These are landed in a more or less putrid state; consequently the oil is unfit for medicinal purposes. It is largely employed in the leather industry. The "unracked" cod oil is recovered by boiling the livers at a somewhat high temperature; this oil contains considerable quantities of "stearine," which is collected, especially in winter, and sold as "fish stearine" for soap-making, or as "fish tallow" for currying. "Norwegian cod oil" and "Newfoundland cod oil" are special brands of cod oil. In consequence of the replacement of steamers for sailing craft, the livers are now brought to shore in a much fresher state than heretofore; hence the quality of cod oil manufactured in this country has greatly improved during the last few years, and approaches more than was formerly the case the quality of Newfoundland cod oil, which owes the preference given to it by tanners to the greater state of freshness in which the livers reached the cod oil extracting works.

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[1] The pale yellow colour is due, according to P. Möller, to a pigment (lipochrome) which is destroyed by the action of bright light (sun-bleached oils).

Physical and Chemical Constants of Cod Liver Oil

Specific Gravity.		
At ° C.		Observer.
15	0·922-0·927	Kremel[1]
,,	0·9247	Bull[2]
,,	0·9326	,, [3]
,,	0·9232-0·9252	,, [4]
,,	0·9217-0·9256	,, [5]
,,	0·9310-0·9410	,, [6]
15·5	0·923-0·930	Allen
,,	0·9249-0·9265	Thomson and Ballantyne
20	0·9202-0·9246	Wijs[9]
99 (water 15·5 = 1)	0·8742	Allen

Solidifying Point.	
° C.	Observer.
0 to – 10	Salkowski

Saponification Value.	
Mgrms. KOH.	Observer.
182-187	Allen
171-189	Kremel
185·1-188·2	Thomson and Ballantyne
175-185	Thoerner
179-193·4	Parry and Sage
183-188[1]	Bull
179·0[5]	,,
168·3-175·2[6]	,,

Iodine Value.	
Per cent.	Observer.
158·7-166·6	Thomson and Ballantyne
153·5-168·4	Parry and Sage
167	Lewkowitsch
135-166·8	,,
135-140·8[3]	Bull
159·7	,,
176·9	Harvey[7]
154·5	,,
181·3	Wijs

Hehner Value.	
Per cent.	Observer.
95·3[1]	Lewkowitsch
96·5[1]	Fahrion

Maumené Test.	
° C.	Observer.
116	Baynes
113	Allen

Specific Temperature Reaction.	
243-272	Thomson and Ballantyne

Refractive Index.		
At ° C.		Observer.
15	1·4800-1·4852	Strohmer
20	1·4769-1·4800	Utz
60	1·4621	Thoerner

Oleo-refractometer.	
" Degrees."	Observer.
+38 to +53 +40 to +46 at 22° C.	Jean Pearmain
+43·5 to +45 at 22° C.	Dowzard[8]

Butyo-refractometer.		
At ° C.		Observer.
15	81·3-86·7	Utz
20	77·5-83·2	,,
25	75	Mansfeld
40	71	,,

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[1] Medicinal oil. [2] Steam liver oil, Lofotes. [3] Japanese steam liver oil, medicinal. [4] Pale oil. [5] Light brown oil. [6] Brown oil. [7] *Journ. Soc. Chem. Ind.* 1902, 694. [8] *Pharmac. Journ. Transact.* (4), 6, 532.

[9] Thirty-four samples of pure cod liver oils of different qualities (*Zeit. angew. Chem.* 1902, 1192).

Physical and Chemical Constants of the Mixed Fatty Acids

Kind of Oil.	Solidifying Point.		Melting Point of *Solid* Fatty Acids.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.		Refractive Index.	
	° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.	At 60° C.	Observer.
	Titer Test.											
Medicinal . . .	17·5-18·4	Lewkowitsch	21-25	Parry and Sage	204·4	Dieterich	287·6-292·5	Parry and Sage	130·5	Thoerner	1·4521	Thoerner
Coast cod . . .	18·7-19·3	,,			207	Thoerner			164·9-170	Parry and Sage		
Norwegian . .	13·3-13·9	,,	(cp. also below, p. 663.)									
Dark, unracked .	22·5-24·3	,,										

P. Möller[1] discerns four qualities of cod liver oil: (1) raw medicinal oil; (2) pale oil; (3) light brown oil; (4) brown oil. As a rule, however, so little is obtained of oil (1) that it is not collected separately.[2]

The commercial "Coast cod oil" is a liver oil obtained from other fish besides cod, such as hake (*Merluccius vulgaris*), haddock (*Merluccius æglefinus*), ling (*Molva vulgaris*), coal fish (*Gadus merlanguss* s. *Komay virens*), in fact any fish that is caught in the nets of the trawlers in the open sea. The livers from these fish are collected in barrels, and usually reach the works of the cod oil extractor in a more or less putrid state, depending on the time that has elapsed after the fish has been caught.

Cod liver oil contains varying quantities of "stearine," according to the temperature at which the oil is recovered. On standing at the ordinary temperature the bulk of the "stearine" settles out. Oils freed from "stearine" are known as "racked" oils (cp. Demargarinated Oils, chap. xv.) Therefore the solidifying point of commercial samples varies considerably.

The chemical composition of the cod liver oil glycerides appears to be very complicated. Since palmitic and stearic acids have been isolated, the occurrence of palmitin and stearin must be accepted as proven. The "stearine" separating from cod liver oil on cooling contains, however, but little true "stearine," *i.e.* glycerides of stearic and palmitic acids. Samples of cod liver oil stearine examined in my laboratory had iodine values ranging from 94 to 102. *Heyerdahl* (evidently in a less carefully prepared specimen) found 113·4. Small quantities of glycerides of the lower saturated fatty acids have been stated by various authors to occur in cod liver oil, such as the glycerides of acetic, butyric, valeric, and capric acids. Thus *Allen* found the *Reichert* values of various samples of oil from 1·1 to 2·1. According to *Salkowski* and *Steenbuch* the volatile fatty acids are secondary products due to the putrefaction of livers, which in the older processes of manufacture always occurred to some extent. The best medicinal liver oils prepared by steam are free from volatile acids.

The nature of the liquid fatty acids in cod liver oil is but imperfectly understood as yet; their high iodine value points to the presence of large proportions of less saturated acids than those belonging to the oleic series. *Fahrion*,[3] examining the liquid fatty acids from a cod liver oil, absorbing 175·5 per cent of iodine, could not identify jecoric acid with certainty. *Fahrion* assumes the presence of an acid, $C_{17}H_{32}O_2$, named by him asellic acid. Nor could he detect physetoleic acid (iodine value = 100), stated by some writers to form the chief constituent of cod liver oil. *Heyerdahl*[4] concluded

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[1] *Codliver Oil and Chemistry*, London, 1895.

[2] Complete details as to the manufacture of cod liver oil in Norway are given in P. Möller's *Codliver Oil and Chemistry*.

[3] *Journ. Soc. Chem. Ind.* 1893, 935.

[4] *Codliver Oil and Chemistry*, p. lxxxix.

that the mixed fatty acids from cod liver oil, freed from its "stearine"—contained amongst other hitherto not identified acids about 4 per cent of palmitic acid, 20 per cent of jecoleic acid (p. 110), and 20 per cent of therapic acid (p. 116). The presence of jecoleic acid is inferred from the existence of dihydroxyjecoleic acid prepared by oxidation of the mixed fatty acids with potassium permanganate, and that of therapic acid from the octobromide $C_{17}H_{26}Br_8O_2$ obtained on brominating the liquid fatty acids. No oleic acid was found in cod liver oil; the "stearine," no doubt, contains some unknown unsaturated acid or acids. In the fresh state cod liver oil is free from hydroxylated acids.

An approximately accurate method for the resolution of the liquid cod liver oil fatty acids consists, according to *Bull*,[1] in the fractional separation of their alkali salts. Cod liver oil is saponified with double normal anhydrous alcoholic potash, and the potassium salts obtained on concentrating the solution are carefully pressed after cooling. The pressed cake is recrystallised from alcohol and pressed again, and the united mother liquors are concentrated, cooled, and pressed, these operations being repeated until a solid potassium salt is no longer obtained. The mother liquors are converted into the sodium salts by isolating the free fatty acids and neutralising them with anhydrous alcoholic soda. The sodium salts are purified in exactly the same manner as described for the potassium salts. The free fatty acids are recovered from the solid salts thus obtained by dissolving the soaps in water in a current of steam, and gradually allowing hydrochloric acid to run on to them, until the solution is distinctly acid. From the alcoholic mother liquors the alcohol is completely removed by distilling in vacuo. The residue is then treated with dry ether until no more passes into solution. Thus the sodium salts of the most unsaturated acids, as also cholesterol, are dissolved. The soaps are recovered from the ethereal solution by washing with water. The soaps insoluble in ether are dissolved in absolute alcohol; by allowing to crystallise, a small amount of a sodium salt may be recovered from the remaining alcoholic mother liquor. The alcohol is finally removed by evaporation and the fatty acids are liberated. Thus the following four groups of fatty acids were obtained:—

A. Fatty acids, the potassium salts of which crystallise from alcohol.
B. Fatty acids, the sodium salts of which crystallise from alcohol.
C. Fatty acid, the sodium salts of which are readily soluble in ether.
D. The remaining fatty acids.

From 1000 grams of cod liver oil *Bull* obtained the following quantities of acids:—

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[1] *Chem. Zeit.* 1899, 996.

Fatty Acids.	Weight.	Neutralisation Value.	Iodine Value.
A.	334 grams	194·2	67·5
B.	375 ,,	190	135·6
C.	120 ,,	167	322·4
D.	69 ,,	169	347

For the conclusions which *Bull* draws from his experiments and for the analytical methods he recommends (all of which stand greatly in need of confirmation[1]), the reader must be referred to the original paper.

On brominating cod liver oil, *Hehner* and *Mitchell* obtained 56·23 per cent of brominated glycerides, to which they ascribed the hypothetical formula, $C_3H_5(C_{18}H_{29}O_2Br_6)(C_{18}H_{29}O_2Br_6)(C_{18}H_{33}O_2Br_2)$. *Walker* and *Warburton* found in my laboratory only 33·7-35·3 per cent of brominated glycerides. From a commercial cod oil, *Hehner* and *Mitchell* obtained 35·5 per cent of brominated glycerides, *Walker* and *Warburton* 30·6-32·7 per cent. The mixed fatty acids of a cod liver oil yielded to *Hehner* and *Mitchell* 18 per cent of a bromide containing 62·91 per cent of bromine (theory requiring for a hexabromo compound 63·31 per cent of bromine). *Walker* and *Warburton*, again, obtained from a genuine cod liver oil, which gave 33·7-35·3 per cent of brominated glycerides, 29·8-30·4 per cent brominated fatty acids. The proportion of bromo compounds no doubt depends on the state of freshness of the sample under examination.

The foregoing notes show that fatty acids of the series $C_nH_{2n-6}O_2$ are present in cod liver oil. The acid of this composition must, however, differ from linolenic acid, since the isolated bromo compounds of the fatty acids do not melt, like linolenic hexabromide, at about 175° C., but remain apparently unchanged until a temperature of 200° C. is reached, when they are converted into a black mass, without however melting to a clear liquid. The difference between the unsaturated acid (or acids) of cod liver oil and the unsaturated acid of the vegetable drying oils is further exemplified by the fact that cod liver oil does not dry to a skin like the vegetable drying oils.

The occurrence of morrhuic acid $C_9H_{13}NO_3$ (differing from tyrosine by H_2) in cod liver oil requires confirmation.

A characteristic constituent of cod liver oil is **cholesterol**. This is isolated by saponifying the oil and exhausting the soap with ether. The residue obtained on evaporating the ether is then crystallised from alcohol, when the characteristic cholesterol crystals are deposited. The quantity of cholesterol in cod liver oil varies, according to *Allen* and *Thomson*, from 0·46 to 1·32 per cent; *Salkowski*[1] gives as an average 0·3 per cent. During the latter years much higher proportions of unsaponifiable matter have been recorded. In view of the fact that the price of cod liver oil has risen considerably, a

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[1] *Jahrbuch der Chemie*, x. 386.

[2] *Zeitsch. f. analyt. Chemie*, 26. 565.

higher proportion of unsaponifiable matter raises the presumption of adulteration with other (liver) oils.

Unsaponifiable Matter in Cod Liver Oils

Description of Oil.	Colour.	Unsaponifiable.	Observer.
		Per cent.	
Steam cod liver oil, medicinal	Pale yellow	0·61	Fahrion[1]
,, ,, ,,	Almost colourless	0·64	,,
,, ,, ,,	Pale yellow	0·98	,,
,, ,, Japan[2] .	...	2·3-2·8	Bull
Medicinal cod liver oil . .	Reddish yellow	0·54	Fahrion
,, ,, . . .	Yellow	1·08	,,
,, ,, . . .	Pale yellow	1·44	,,
,, ,, . . .	Yellow	0·87	Thomson and Ballantyne
Commercial oil, yellow . .	,,	0·65	Fahrion
,, ,, ,, . .	,,	1·18	,,
,, ,, English .	Yellowish red	2·62	,,
,, ,, ,, .	Pale yellow	0·6-0·78	Lewkowitsch
,, ,, Newfoundland	Reddish brown	1·50	Thomson and Ballantyne
Brown cod oil[3] . . .	Brown	1·82	Fahrion
,, ,, . . .	,,	2·23	,,
,, ,, ...	,,	2·68	,,
,, ,, ...	,,	1·87	Thomson and Ballantyne
,, ,, ...	,,	7·3 (!)	Bull

Raw medicinal oil, *i.e.* the first oil exuding spontaneously from the livers, contains very small quantities of ptomaïnes (*Heyerdahl*). In light brown cod liver oil, however, organic bases occur to the extent of from 0·035 to 0·050 per cent (*Gautier* and *Morgues*).[4] The following bases have been isolated :—

Bases in Cod Liver Oil

Volatile.	Non-volatile.
Butylamine	Morrhuine, $C_{19}H_{27}N_3$
Isoamylamine	Aselline, $C_{25}H_{32}N_4$
Hexylamine	
Dihydrolutidine	

Since these bases are determined as unsaponifiable matter together with the cholesterol, the large amounts of unsaponifiable matter

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[1] *Journ. Soc. Chem. Ind.* 1893, 607.

[2] Mann (*Journ. Soc. Chem. Ind.* 1903, 1357) records 7·18 per cent of unsaponifiable matter for an oil of the saponification value 186·7 (!).

[3] Bull found 7·3-7·9 per cent of unsaponifiable matter in some brown oils. These figures suggest the presence of other liver oils.

[4] *Compt. rend.* 107, 251 ; 626 ; 740.

recorded by some observers would seem to be due to an excessive amount of these bases in some specimens of oil.

Heyerdahl has isolated *trimethylamine* by means of its platinochloride. This base, however, must, like those mentioned above, be considered as a product of decomposition of the cellular tissue of the livers. Biliary colouring matters, stated to occur by earlier observers, are absent. According to *Salkowski* the colouring principle in cod liver oil belongs to the class of *lipochromes.*

Small quantities of albuminoid substances occurring in cod liver oil must also be considered as secondary products. According to *Unger*,[1] minute quantities of *iron*, *manganese*, and *phosphoric acid* are chemically combined with the albuminoids (a substance similar to lecithin, yielding phosphoric acid, glycerol, and the above-mentioned morrhuic acid, has been obtained by *Gautier* and *Morgues*). Also *calcium*, *magnesium*, and *sodium* have been found, and further, chlorine, bromine, and iodine. The following amounts of iodine have been recorded :—

Proportion of Iodine in Cod Liver Oil

Description of Oil.	Iodine. Per cent.	Observer.
Pale . . .	0·020	Andrès
Yellow . . .	0·031	,,
...	0·00138-0·00434	Stanford
...	0·0002	Heyerdahl

Formerly the *therapeutic value* of cod liver oil was ascribed to the small amount of iodine it contained (therefore cod liver oils are met with to which iodine or potassium iodide has been added fraudulently), or to any of the many "active principles" stated by several writers to occur in cod liver oil. Thus *Marpmann*[2] describes a substance which is precipitated by ether and alcohol, and is said to cause the cod liver oil to become completely emulsified on coming in contact with the gastric juice. The medicinal effect of cod liver oil, however, must rather be looked for in the facility with which it is hydrolysed or digested, and it cannot be doubted that this property is caused by the peculiar constitution of its unsaturated fatty acids. From the medicinal point of view that cod liver oil is the best which has been prepared from fresh livers and kept protected from the action of light and air.

Heyerdahl has studied the influence which the length of time during which the livers are heated has on the proportion of free fatty acids in the oil produced. He found, contrary to expectation, that the percentage of free fatty acids decreased slightly but perceptibly as the time of heating was increased (from 20 to 80 minutes) and the temperature was allowed to rise (from 62° to 85° C.). This result may be ascribed to the volatilisation of free volatile acids at the

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[1] *Pharmac. Centr.-Halle*, 1889, 261.

[2] *Chem. Centr. Blatt.* 19. 1213.

higher temperature, or to the fact that the first portions of the extracted oil were richer in fatty acids, or to both causes conjointly. Experiments, in which measured volumes of air were driven through samples of oil heated in the water-bath, proved that the free fatty acids decreased up to a certain point, and then slowly rose to or beyond the original percentage. The proportions of free fatty acids never exceeded 0·69 per cent, calculated as oleic acid.

The oil obtained by passing steam directly into the livers is, according to the same chemist, practically devoid of volatile fatty acids; their occurrence in commercial oils must therefore be due to some secondary process. This statement has been corroborated by the examination of liver oils from other species of fish (*Heyerdahl*).

How far the oil may thus be affected is shown by the numbers contained in the following table:—

Free Fatty Acids in Cod Liver Oils, calculated as Oleic Acid

Description of Oil.	Colour.	Acid Value.	Free Fatty Acids.	Observer.
			Per cent.	
Raw medicinal oil	Pale	7·38	3·79	Heyerdahl
,, ,,	Somewhat darker	7·55	3·87	,,
,, ,,	Darkest	7·72	3·96	,,
Pale oil } obtained from	Pale	21·20	10·9	,,
Brown ,, } livers by decay	Brown	54·4	28·0	,,
Medicinal oil	Yellow	...	0·36	Thomson and Ballantyne
Scotch cod oil	Brown	...	9·73	,,
Newfoundland cod oil	Red-brown	...	23·31	,,
Medicinal oils	...	...	0·34-0·60	Parry and Sage

Examination of Medicinal Cod Liver Oil.—For the valuation of medicinal cod liver oil, the acid value, iodine value, and the Reichert-Meissl value will furnish the most valuable indications.

The proportion of *free fatty acids* should be as small as possible. No definite limit can be laid down, but a comparison with the numbers recorded in the last table will afford the necessary guidance. It may therefore suffice to state that the best steam cod liver oils contain from 0·3 to 1·5 per cent of free fatty acids (calculated to oleic acid), whereas medicinal oil prepared by older processes exceeds this number, and may reach as much as 3 or even more per cent.

The *Reichert-Meissl* value should be low and should not exceed 0·5. A higher number would indicate that the livers employed for extraction had not been fresh.

The higher the *iodine value*, the less oxidation can have taken place, and if the medicinal properties be valued by the amount of unsaturated fatty acids, then the higher the iodine value the better the oil. The mean iodine value of a good medicinal oil may be taken as 167. Since, however, the magnitude of the iodine value depends on the extent to which the "stearine" has been removed, it would not be permissible, without further examination, to declare samples having lower iodine values as adulterated.

The amount of *unsaponifiable matter* should not as a rule exceed 1·5 per cent (cp. table, p. 666). Larger amounts would point (in the absence of mineral oils) to admixture with other liver oils such as shark liver oils, which contain notable proportions of spermaceti, or even of liver oils from *Merlangus* (Sej liver oil), which is largely substituted for cod liver oil.

The following table shows the proportions of unsaponifiable matter found in some liver oils other than cod liver:—

Liver Oils.		Unsaponifiable.	Observer.
		Per cent.	
Shark liver oil .	Yellow, steamed	5·27	Fahrion
,,	Red	4·44	,,
,,	Yellow	1·24	,,
,,	Yellowish-red	0·93	,,
,,	Japanese	2;82	Allen
,,	Crude	8·70	,,
,,	Refined	0·70	,,
		10·25	,,
		17·30	,,
		10·34	,,
,,	Pale yellow, from *Scymnusborealis*	10·20	Lewkowitsch
,,	Japanese shark	14·4-21·5	Bull
Coalfish ,,	...	6·52	Mann
Tunny fish ,,	...	1·0-1·8	Fahrion
Ling liver ,,	...	2·23	Bull
Haddock ,,	...	1·1	Lewkowitsch

Adulteration with mineral oils is readily ascertained by the determination of the saponification value and of the unsaponifiable matter, and the examination of the latter. Adulteration with vegetable oils is best detected by the phytosteryl acetate test, as the iodine value obviously does not furnish decisive results, although it may give the first indications, if adulteration with oils having iodine values of less than 120 has taken place.[1] Confirmation of the presence of vegetable oils other than linseed oil may also be obtained by the hexabromide test. In this connection it should be noted that cod liver oil substitutes are now being sold consisting of a mixture of genuine cod liver oil and iodised sesamé oil (Iodipin, chap. xv.). Such artificial cod liver oils will yield much less hexabromide than a genuine oil.

In consequence of the high prices that rule at present for cod liver oil, adulteration with other liver oils, fish oils, and blubber oils is practised extensively, and frequently fish oils and blubber oils are fraudulently sold as cod liver oil. The detection of other liver oils in cod liver oil constitutes, in the present state of our knowledge, a very

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[1] A cod liver oil substitute is sold under the name of "*Fucol*"; it is prepared by digesting marine algæ with a vegetable oil (*Zeit. ang. Chem.* 1904, 397).

difficult problem. The determination of the unsaponifiable matter would appear to afford some guidance as to adulteration with other liver oils.

The hexabromide test would also appear to lead to useful results, since the examination of shark liver oil in my laboratory has shown that the fatty acids yielded from 12·7 per cent to 15 per cent of insoluble bromide only, as against 30 per cent in the case of genuine cod liver oil.

Since the discrimination of fish and blubber oils from cod liver oil is not always possible by means of quantitative reactions, a number of *colour tests* have been recommended. I have examined the tests proposed by *Kremel*, *Meyer*, *Roessler*, and *Unger*,[1] but as I have found them useless, they are not described here. The colour test, however, described on p. 659, allows to differentiate fish and blubber oils from liver oils. Also the following colour reactions permit to distinguish fish and blubber oils from liver oils.

Pure cod liver oil gives in the *Hager-Salkowski* cholesterol test (p. 140) at first a violet-blue, then purple, then brownish-red colour, changing at last into a deep brown. According to *Salkowski* these colourations are not only due to cholesterol, but also to a lipochrome and to the cod liver oil acids themselves. For if the unsaponifiable matter isolated from cod liver oil be dissolved at once in chloroform, without separating the cholesterol by crystallisation from alcohol, a clear, golden-yellow solution is obtained, giving a beautiful indigo-blue colour with sulphuric acid in the first instance, and afterwards the cholesterol reaction. The blue colour is due to a lipochrome.

The *German Pharmacopœia* prescribes the following colour test:—Dissolve one drop of oil in twenty drops of carbon bisulphide, and add one drop of concentrated sulphuric acid, when a beautiful violet-blue colour appears at once, changing afterwards into red and brown. This test, however, cannot serve as an identity reaction, since other liver oils give the same *violet-blue* colour. Cod liver oil, as also other liver oils which have become rancid, do not show the violet-blue, but give at once the red colouration.

The detection of fish and blubber oils that have been fraudulently admixed in smaller or larger quantities with cod liver oil is, in the present state of our knowledge, still an unsolved problem. Seal and whale oil yield much smaller proportions of hexabromides than cod liver oil, as has been ascertained by *Walker* and *Warburton* in my laboratory. But Japan fish oil and a deodorised fish oil have given numbers ranging from 23 per cent to 39 per cent of insoluble bromides, so that it is easy to prepare mixtures of cod liver oil, fish oil, and blubber oil yielding the average percentage of hexabromides furnished by the genuine cod oil. At present exact methods for the detection of these adulterants are still wanting.

For the determination of the amount of **iodine** in cod liver oil or iodised cod liver oil, *Stanford*[2] proposed to saponify 300 grms. of oil

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[1] See second edition of this work, p. 486. Cp. also Wiebelitz, *Pharm. Zeit.* 1903, 363.

[2] *Pharm. Journ.* (3) 14. 353.

Lesser Known Liver Oils

Liver Oil from	French.	German.	Italian.	Source.	Specific Gravity.	Saponification Value.	Iodine Value.	Hehner Value.	Oxidised Acids.	Mean Molecular Weight of Mixed Fatty Acids.	Acetyl Value.	Acid Value.	Unsaponifiable. Per cent.	Observer.
									Per cent.					
Skate	...	Meerengelleberoel	Olio di fegato di squadro angelo	Squatina vulgaris	0·9307 (at 15° C.)	185·4	157·3	94·7	...	...	10·6	...	0·97	Lewkowitsch
Tunny	Huile de foie de thon	Thunfishleberoel	Olio di fegato di tonno	Thynnus vulgaris	...	...	155·9	95·79	3·11	290	...	0·2-34	1·0-1·8	Fahrion
Haddock [1]	..	Schellfischleberoel	...	Merluccius æglefinus	0·9298 (at 15° C.)	188·8	154·2	93·3	...	...	...	...	1·1	Lewkowitsch
Coal fish [2]	Huile de foie de merlan	Sejleberoel	Olio di fegato di merlango	Gadus merlangus (virens)	0·925 (at 15° C.) 0·9272	177-181 186·1	123-137 [3] 137-162 139·1	...	...	...	...	1·26-1·68 7·2 ; 21·6 2·8	... ... 6·52	Kremel Bull Mann
Ling	Huile de foie de lingue	Lengleberoel	...	Molva vulgaris	0·9200 (at 15° C.)	184·1	132·6	...	...	...	...	10·9	2·23	Bull
Shark (Arctic)	Huile de foie de requin	Haifischleberoel	Olio di fegato di pesce cane	Scymnus borealis	0·9163 (at 15° C.)	161·0	114·6	86·9	...	...	11·9	...	10·2 [4]	Lewkowitsch
,, ,,	...	...	...	...	0·9105-0·9130	146·1-148·5	111·9-114·9	...	...	...	...	2·6-6·2	20·8-21·8	Bull
,, (Japan)	..	...	...	...	0·9156-0·9177	163·4-163·5	128·3-136	...	...	...	...	0·88-1·5	14·4-21·5	,,
,, ,,	...	...	...	...	0·9158	157·2	90	...	...	...	...	...	...	Eitner
Ray	Huile de foie de raie	Rochenleberoel	Olio di fegato di razza	Raja clavata (batis)	0·9280 (at 15·5° C.)	...	...	...	...	...	...	...	...	...
Hake	...	Seehechtleberoel	Olio di fegato de luccio marino	Merluccius communis (vulgaris)	0·9270 (at 15·5° C.)	...	...	...	...	...	...	...	...	...

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[1] This oil is frequently termed cod liver oil, especially in the French and Italian literature.

[2] This is the Danish "Sejthran" or "Sejleberthran."

[3] Older observations by Kremel (*Pharm. Centr. Halle*, 1884, 337) led to 123-137.

[4] Cp. also table, p. 669.

with 40 grms. of caustic soda (free from iodine), then to evaporate to dryness and incinerate the soap in a porcelain crucible. The charred mass is then boiled out with water, filtered, and the filtrate evaporated to 300 c.c. 30 c.c. of this solution are then shaken with 12 c.c. of carbon bisulphide after a few drops of nitrosulphuric acid have been added (prepared by passing nitrous acid, evolved on heating starch or arsenious acid with nitric acid, into sulphuric acid). The amount of iodine dissolved in the carbon bisulphide is then estimated colorimetrically by comparing the tint with that of another solution prepared similarly from a known amount of potassium iodide.

On shaking pure cod liver oil with water or alcohol no iodine passes into solution; fraudulently added potassium iodide can therefore thus be detected.

In the examination of commercial cod oil for tanning and currying purposes, the amount of free fatty acids and unsaponifiable matter does not play the same important part as in the examination of medicinal oil.

Other liver oils are commercially of minor importance, and therefore need not be considered here individually. In the following table I collate the characteristics of some liver oils. Shark liver oil appears to be no longer used in this country; at any rate it is not extracted here commercially. This oil is prepared in considerable quantities in Iceland, and exported to the Continent for use in tanning; it is also manufactured at the coast of California, the coarser grades being used in the making of tarpaulins and other oiled cloth. The livers from any shark caught by the trawlers are extracted together with other livers, and therefore the "Coast Cod Oil" (p. 663) will contain varying quantities of shark liver oil.

Lesser known liver oils, see table opposite.

γ. Blubber Oils

In this group I comprise oils of different composition. Seal oil, whale oil, turtle oil, and dugong oil consist almost wholly of glycerides; dolphin oil and porpoise oil contain notable amounts of spermaceti, forming, as it were, intermediate members between true fatty oils and liquid waxes.

The last two members of this group, dolphin and porpoise oils, occupy an exceptional position on account of their containing considerable proportions of glycerides of volatile acids. In this respect turtle and dugong oils form intermediate links between these two oils on the one hand, and seal and whale oils on the other.

SEAL OIL

French—*Huile de phoque.* German—*Robbentran, Seehundstran.*
Italian—*Olio di foca.*

For tables of constants see pp. 673, 674.

Seal oil is the oil obtained from the blubber of the various species of the seal, such as *Phoca vitulina*, *Phoca grœnlandica*, *Phoca lagura*, *Phoca caspica*, etc.

According as the oil is extracted from fresh blubber on board the steamer, or from blubber which has been brought to shore, the colour of seal oil varies. In commerce we find four brands of seal oil—water-white, straw seal, yellow seal, and brown; these represent the oils as they are obtained successively by rendering the oil from the blubber. The darkest quality is that which has been the longest in contact with the animal tissue, and has been extracted at the highest temperature.

According to *Ljubarsky*[1] the mixed fatty acids from the Caspian seal consist roughly of 17 per cent palmitic acid and 83 per cent of liquid acids. The latter yielded on oxidation a mixture of dihydroxypalmitic and dihydroxystearic acids, from which the presence in the original oil of oleic acid and physetoleic acid (or hypogæic acid) was inferred. *Ljubarsky* found no linolic acid in the oil, the presence of which had been recorded by *Kurbatoff.*[2]

Walker and *Warburton* obtained, however, in the hexabromide test 27·54-27·92 per cent of ether-insoluble brominated glycerides; the fatty acids yielded only 19·8-19·9 per cent of insoluble bromide, which behaved like the brominated products obtained from fish and liver oils.

Bull isolated from a specimen of northern seal oil a liquid fatty acid absorbing 306·8 per cent of iodine.

In the claïdin test seal oil gives a pasty mass which separates from a liquid portion.

The following table records the proportions of free fatty acids and unsaponifiable matter found by several observers:—

No.	Kind of Seal Oil.	Free Fatty Acids (as Oleic Acid).	Unsaponifiable Matter.	Observer.
		Per cent.	Per cent.	
1	...	1·95	...	Deering
2	...	2·01	...	,,
3	Cold-drawn, pale .	1·80	0·5	Thomson and Ballantyne[3]
4	Steamed, pale .	1·46	0·38	,,
5	Tinged (brown) .	8·29	0·42	,,
6	Norwegian . .	7·33	0·51	,,
7	Northern . .	3·2	1·05	Bull
8	Very pale . .	0·98-1·13	...	Chapman and Rolfe[4]
9	Yellow . . .	1·41	...	,,
10	Light brown .	4·09	...	,,
11	Dark brown . .	19·95	...	,,

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[1] *Journ. f. prakt. Chemie*, 1898, 26.

[2] *Berichte*, 25, Referate 506.

[3] *Journ. Soc. Chem. Ind.* 1891, 236.

[4] *Ibid.* 1894, 843.

Physical and Chemical Constants of Seal Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.	
°C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
15	0·925	Kremel	Deposits "stearine" at 3	Schaedler	189-196	Stoddart, Deering	127-128	Kremel
,,	0·9249-0·9263	Chapman and Rolfe					142·2-152·4	Thomson and Ballantyne
15·5	0·9240-0·929	Allen	− 2 to − 3	Jean	178-179	Kremel	130·6	Lewkowitsch
,,	0·9244-0·9261	Thomson and Ballantyne			189·3-192·8	Thomson and Ballantyne	129·5-141 [1]	Chapman and Rolfe
99	0·8733	Allen			190·7-196·2	Chapman and Rolfe	147·1	Bull

Physical and Chemical Constants of Seal Oil—continued

Reichert Value.		Hehner Value.		Maumené Test.		Refractive Index.	
						Oleo-refractometer.	
c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.	"Degrees" at 22° C.	Observer.
0·07-0·22	Chapman and Rolfe	95·45 92·8-94·2	Kremel Chapman and Rolfe	92	Allen	+8 +15 +30 to +36 +32	Jean ,, Pearmain Dowzard
				Specific Temperat. Reaction.			
				212-229	Thomson and Ballantyne		

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[1] The bromine values of the specimens were 69·6-80, corresponding to iodine values 110·5-126·7.

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Neutralisation Value.	
°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.
Titer Test. 15·5-15·9	Lewkowitsch	22-33	Chapman and Rolfe	190·4-196	Chapman and Rolfe

The best qualities of seal oil are used as burning oils in lighthouses, or as an adulterant of cod liver oil; lower qualities of seal oil are used in soap-making. Seal oil in its turn is largely adulterated with mineral oils and rosin oils, the detection of which is, however, easy. A mixture of seal oil with various fish oils is frequently sold as seal oil. The detection of the adulterant is not easy, as neither the iodine value nor the hexabromide test furnish decisive indications. In the present state of our knowledge the taste and smell alone render some assistance in the examination.

WHALE OIL

French—*Huile de baleine.* German—*Walfischtran.*
Italian—*Olio di balena.*

For tables of constants see pp. 676, 677.

Whale oil is the oil extracted from the blubber of various species of the genus *Balæna*, as *Balæna mysticetus*, Greenland or "Right" whale (Northern whale oil), *Balæna australis* (Southern whale oil), *Balænoptera longimana*, *Balænoptera borealis* (Fin-back oil, Finner whale oil, Humpback oil: French—*Huile de rorqual;* German—*Finnfischtran*). The northern whale oil is the "train oil" proper; but this name has become a generic name, and has been extended to all other "blubber oils" included in this group. (See Appendix.)

The whale caught by the whalers in the northern seas is no longer worked up on board the vessels, but is brought into the "trying" stations situated in Finnmarken and on the Lofotes and in Iceland. According to the equipment of the blubber-rendering stations, the yield of the oil and also its quality vary. In the most modern works the blubber is stripped clean from flesh immediately after the arrival of the whaler, and care is taken to leave as little flesh as possible on the blubber. The latter is then cut into strips, which are thrown into chopping machines, whence the comminuted mass is immediately delivered into melting pans, and boiled with steam. Five different qualities of whale oil are produced. The best quality is the oil which first runs off the blubber at the lowest temperature, known in commerce as "Whale Oil No. 0"; it is of a pale yellow colour, and has but a faintly fishy smell. This oil contains a very small quantity of free fatty acids. The best brands are water-white, and are free from volatile fatty acids. On further boiling, the second quality ("Whale Oil No. 1") runs off; it is a little darker in colour, although still pale yellow. Its fishy smell is more pronounced than the oil of the first running.

These two qualities of oil are stored in large vessels, whereby they become clarified and deposit "stearine," which is sold as "whale tallow" for soap-making.

The residual mass in the boiling pans, together with the flesh of the whale, is cut up into strips or fairly large lumps, and is "tried down" in a digester under a pressure of 40-50 lbs. Thus the oil classed "No. 2 oil" is obtained. This oil has a brown colour and a strongly developed fishy smell; its proportion of fatty acids is considerably higher than in "Oil No. 1."

The bones are also worked up in the same manner, and yield a still inferior quality of oil. Such oil ("Whale Oil No. 3") is darker still, has a more strongly developed odour, and a high percentage of free fatty acids.

The oil obtained after the flesh has undergone some pronounced putrefaction ("Whale Oil No. 4"), is still darker, and more objectionable as regards smell and fatty acids. In the lowest three qualities the proportion of unsaponifiable matter is somewhat considerable.

The following table gives some characteristics of various brands of whale oil. The numbers are due to *Bull*:—

	Specific Gravity at 15° C.	Acid Value.	Saponific. Value.	Iodine Value.	Unsaponifiable.
Antarctic right whale oil (America)	0·9257	0·56	183·1	136·0	1·46
Whale oil No. 1, unrefined (Finnmarken)	0·9181	0·86	188·6	104·0	2·36
Refined (Glasgow) . .	0·9214	1·4	184·7	113·2	2·33
Arctic whale oil, refined (America)	9·9234	1·9	185·0	117·4	2·11
Crude white whale oil (America)	0·9222	2·5	183·9	127·4	1·37
Whale oil No. 2, unrefined (Finnmarken)	0·9182	3·6	188·3	...	3·3
Yellow whale oil, refined (Glasgow)	0·9232	10·6	185·9	110·0	1·89
Whale oil No. 3, refined (Finnmarken)	0·9162	26·5	185·7	96·0	2·42
Brown whale oil, refined (Glasgow)	0·9272	37·2	160·0	125·3	3·22
Whale oil No. 4, unrefined (Finnmarken)	0·9205	58·1	182·1	89·0	3·4
Dark whale oil, refined (Glasgow)	0·9170	98·5	178·3	103·1	3·03

Physical and Chemical Constants of Whale Oil

Specific Gravity.			Saponific. Value.		Iodine Value.		Reichert Value.		Hehner Value.		Maumené Test.		Refractive Index. Oleo-refractometer.	
° C.		Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	° C.	Observer.	" Degrees."	Observer.
15	0·9170-0·9272	Bull	193·1[1]	Deering	110·1	Thomson and Ballantyne	0·7-2·04	Lewkowitsch	93·5	Lewkowitsch	91[3]	Allen	+30·5	Jean
15·5	0·9307	Allen	188·5-224·4	Stoddard, Allen							85-86[1]	Dobb	+42 to +48	Pearmain
"	0·9221-0·9225	Schweitzer and Lungwitz	188·8	Thomson and Ballantyne	121·3-127·7	Schweitzer and Lungwitz					92[1]	Archbutt		
											61	Jean		
15	0·9193	Thomson and Ballantyne	188·5	Lewkowitsch	136·0[2]	Bull								
98·99	0·8725	Allen	187·9-194·2	Schweitzer and Lungwitz										
											Specific Temperature Reaction.			
											157	Thomson and Ballantyne		

[1] Southern whale oil.

[2] Antarctic right whale.

[3] Northern whale oil.

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.		Solidifying Point.		Melting Point.		Iodine Value.	
At 100° C. (Water 100° C.=1.)	Observer.	° C.	Observer.	° C.	Observer.	Per cent.	Observer.
0·8922	Archbutt	Titer Test.		27	Jean	130·3-132	Schweitzer and Lungwitz
		22·9-23·9	Lewkowitsch	14-15 16 16·2 18	Schweitzer and Lungwitz	Liquid Fatty Acids.	
						144·7	Clapham[1]

The chemical composition of the whale oil fatty acids has not yet been established satisfactorily. The deposited "stearine" consists to a large extent of palmitin. Volatile fatty acids are absent; the high *Reichert* values recorded by earlier observers are undoubtedly due to the specimens examined having become rancid.

Hehner and *Mitchell* obtained from a specimen of whale oil 25 per cent of a brominated glyceride, to which they ascribed the composition $C_3H_5(C_{18}H_{30}O_2Br_6)_2(C_{18}H_{33}O_2Br_2)$. A specimen of whale oil examined in my laboratory by *Walker* and *Warburton* gave only about 16 per cent of a hexabrominated glyceride, whilst the fatty acids yielded 12·4 per cent of a (hexa ?) brominated acid, which behaved like the products derived from other marine animal oils, in that it blackened at 200° C. without melting. *Bull* isolated from a number of whale oils some highly unsaturated fatty acids, having iodine values ranging from 251 to 315·6. The readiness with which low class whale oils become oxidised on exposure to the air may explain the fact that *Fahrion* found from 0·39 to 1·44 per cent of oxidised fatty acids in some specimens.

The amount of unsaponifiable matter also varies with the quality of the oil. The following table contains the amounts of unsaponifiable matter determined in commercial oils. The lower the quality of the oil, the larger the amount of unsaponifiable matter, and the lower will consequently be the saponification value.

Unsaponifiable Matter in Whale Oils

Description of Oil.	Per cent.	Observer.
Norwegian, yellowish-red .	0·65	Fahrion
,, yellowish-brown .	1·26	,,
,, brown . .	1·37	,,
Pale	1·22	Thomson and Ballantyne
,, refined	0·92-3·72	Lewkowitsch
Samples described in table, p. 675	1·4-3·4	Bull

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[1] Determined in the writer's laboratory.

The iodine value of a given specimen of whale oil depends on the amount of "stearine" left in the oil; hence the great variations in the numbers recorded in the tables are readily explained.

Whale oil is largely adulterated with rosin oil, the detection of which is simple. More difficult is the detection of admixed seal oil, on account of the great similarity of the two oils; at present this is practically impossible by chemical means, taste alone permitting the recognition of the seal oil.

The water-white and pale brands of whale oil are used as burning oil and in soap-making. The lower qualities are employed for leather-dressing.

TURTLE OIL[1]

French—*Huile de tortue.* German—*Schildkrötenoel.*
Italian—*Olio di tartaruga.*

This oil is the body-fat from *Thalassochelys corticata*, for which the following characteristics have been ascertained.

Physical and Chemical Constants of Turtle Oil

Specific Gravity at 42·5° C.	Solidifyng Point. °C.	Melting Point. °C.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.
0·9198	10·0	23·27	209	112	4·6

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point. °C.	Melting Point. °C.	Mean Molecular Weight.	Iodine Value.
28·2	30·2	268	119

The specimen examined had the acid value 0·57.

DUGONG OIL, MANATEE OIL

French—*Huile de lamantin.* German—*Dugongoel.*
Italian—*Olio di vacca marina.*

This oil is obtained from the blubber of the sea-cow (*Halicore australis* and *Halicore indicus*), a mammal living near the shores of the Indian Archipelago.

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[1] Zdarek. *Zeit. f. physiolog. Chem.* 1903, 460.

Physical and Chemical Constants of Dugong Oil

Specific Gravity at 60° F.	Saponific. Value. Mgrms. KOH.	Iodine Value. Per cent.	Reichert Value. c.c. $\frac{1}{10}$ norm. KOH.
0·9203	197·5	66·6	2·5

The specimen of dugong oil examined by *Mann*[1] gave the numbers recorded in the table. This specimen is stated to contain 3·74 per cent of unsaponifiable matter and 2·39 per cent of free fatty acids.

DOLPHIN OIL, BLACKFISH OIL

French—*Huile de dauphin.* German—*Delphintran.*
Italian—*Olio di delfino.*

For table of constants see p. 680.

Dolphin oil, from the blubber of the blackfish (bottlenose dolphin), *Delphinus globiceps*, forms an intermediate link between whale oil (consisting nearly wholly of glycerides) and sperm oil (a true wax).

The yield of oil from the blubber of a dolphin averages from one-sixth to four barrels of 31·5 gallons.

This oil is of a pale yellow colour. On standing it deposits spermaceti (cetyl palmitate) [*Chevreul*]. *Bull*[2] found amongst the liquid fatty acids 14·3 per cent of an acid having the iodine value 285·5 and the neutralisation value 313·2. The oil is remarkable on account of the large amount of glycerides of volatile fatty acids it contains, a characteristic which it shares with porpoise oil. *Bull* isolated from a specimen of body oil 2·01 per cent of unsaponifiable matter.

Larger still is the proportion of glycerides of volatile acids in the *jaw oil*, the oil from the soft blubber contained in the head and jaw of the blackfish. The *jaw oil*, "melon oil,"[3] has a straw-yellow colour and a not unpleasant smell. It is used for lubricating fine machinery, such as watches and type-writing machines.

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[1] *Journ. Soc. Chem. Ind.* 1903, 1357.

[2] *Chem. Zeit.* 1899, 1044.

[3] Cp. Archbutt and Deeley, *Lubrication and Lubricants*, p. 115.

[Table

Physical and Chemical Constants of Dolphin Oil

	Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Reichert Value.		Hehner Value.		Refractive Index.		
	At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	At °C.		Observer.
Body oil	15	0·9266	Bull	Deposits spermaceti from 5 to − 3	Schaedler	197·3 203·4	Moore Bull	99·5 126·9	Moore Bull	5·6	Moore	93·07	Moore[1]	15 20	1·4708 1·4682	Utz ,,
Jaw oil						290	Moore	32·8	Moore	65·92	Moore	66·28	Moore	Butyro-refractometer.		
														At °C.	"Degrees."	Observer.
														15 20	67·7 63·6	Utz ,,

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[1] *Journ. Soc. Chem. Ind.* 1890, 331.

PORPOISE OIL

French—*Huile de Marsouin.* German—*Meerschweintran.*
Italian—*Olio di porco marino.*

For table of constants see p. 682.

Porpoise oil is obtained by boiling the whole tissue of the brown porpoise, *Delphinus phocæna* with water. This oil has been examined first by *Chevreul*, who discovered in it valeric acid, named by him "acide phocénique." On account of its somewhat high proportion of unsaponifiable matter, it seems to form an intermediate link between the blubber oils and the liquid waxes.

The oil is pale yellow. It consists of the glycerides of valeric, palmitic, stearic, and oleic (and physetoleic ?) acids. This oil also is sold commercially in two varieties, as a body oil and as a jaw oil. The body oil is pale yellow and resembles the dolphin body oil. The jaw oil also simulates the corresponding dolphin oil in its composition.

The jaw oil is easily soluble in alcohol at 70° C.; it is therefore possible to extract it from a mixture of the body and jaw oils. The specimen of body oil examined by *Bull* contained 3·7 per cent of unsaponifiable matter. *Bull* isolated 19·48 per cent of fatty acids having the iodine value 322·5 and the neutralisation value 191·4. In a specimen of porpoise jaw oil *Bull* found 16·4 per cent of unsaponifiable matter, and 21·13 per cent of fatty acids having the iodine value 31·3 and the neutralisation value 367·8. This points to large proportions of (iso)valeric acid.

The oil is used, like dolphin oil, for lubricating purposes.

[TABLE

Physical and Chemical Constants of Porpoise Oil

	Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.		Reichert Value.		Hehner Value.		Maumené Test.	
	° C.		Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	° C.	Observer.
Body oil	15	0·9258	Bull	– 16	Schaedler	216-218·8	Allen	119·4	Bull	11-12	Allen			50	Allen
	15·5	0·926	Allen			195	Bull			23·45[1]	Steenbuch[3]				
	16	0·937	Chevreul												
	99 (water 15·5=1)	0·8714	Allen												
Jaw oil, skimmed and strained	15	0·9258	Bull			253·7	Moore	49·6	Moore	47·77	Moore	72·05	Moore[2]		
						272·3	,,	30·9	,,	56·00	,,	68·41	,,		
						269·3	Bull	21·5	Bull	65·8[1]	Steenbuch				
Jaw oil, not skimmed nor strained						143·9	Moore	76·8	Moore	2·08	Moore	96·5	,,		

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[1] Reichert-Meissl values 46·9 and 131·6 halved for the sake of comparison.

[2] *Journ. Soc. Chem. Ind.* 1890, 331.

[3] *Zeit. angew. Chem.* 1899, 64.

(2) TERRESTRIAL ANIMAL OILS

In addition to the oils obtained from the feet of oxen, sheep, and horses, and from eggs, the liquid fats obtained from lard and tallow by pressing would fall under this head. The last two oils are, however, more suitably described in connection with the raw material from which they are derived.

The terrestrial animal oils are characterised by a low iodine value, lower than that of the non-drying vegetable oils, and low thermal reactions. They yield solid elaïdins with nitrous acid; they are readily differentiated from vegetable oils by means of the phytosteryl acetate test.

SHEEP'S FOOT OIL

French—*Huile de pieds de mouton.* German—*Hammelklauenoel, Schafpfotenoel.* Italian—*Olio di piede di montone.*

For tables of constants see p. 684.

This oil is obtained from sheep's trotters in the manner described for neat's foot oil (see p. 687). The sample examined by the author (see table) was prepared in the laboratory from sheep's trotters.

Sheep's foot oil much resembles neat's foot oil, and is, as a rule, sold as neat's foot oil.

Physical and Chemical Constants of Sheep's Foot Oil

Specific Gravity.		Solidifying Point.		Saponification Value.		Iodine Value.		Maumené Test.		Refractive Index.	
										Oleo-refractometer.	
At 15° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	° C.	Observer.	"Degrees."	Observer.
0·9175	Schaedler	0 to 1·5	Schaedler	194·75[1]	Lewkowitsch	74-74·4[1]	Lewkowitsch	49·5	Jean	0[2]	Jean

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point. Titer Test.	
° C.	Observer.
20·0-21·1[1]	Lewkowitsch

---

[1] Specimen prepared in the laboratory.

[2] Sheep's foot oil is the standard oil for Jean's oleo-refractometer.

HORSES' FOOT OIL

French—*Huile de pieds de cheval.* German—*Pferdefussoel.*
Italian—*Olio di piede di cavallo.*

For tables of constants see p. 686.

This oil is obtained from horses' feet.

It is not met with in commerce under its true name, and what is described as horse oil is more or less the liquid portion of horse fat. The horses' feet are usually boiled out together with neat's feet and sheep's feet, and the resulting oil is indiscriminately sold as neat's foot oil, or at least as "animal" oil.

The specimen rendered in my laboratory contained, even after filtering, certain impurities, so that the oil gave several colour reactions which have been previously considered as characteristic of marine animal oils (cp. p. 651). The oil had a high acetyl value, viz. 9·1-10·3 due to changes caused by the contact of the oil with organic impurities.

[Table

Physical and Chemical Constants of Horses' Foot Oil

Specific Gravity.			Saponification Value.		Iodine Value.		Maumené Test.	
At °C.		Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	°C.	Observer.
15	0·9202-0·9205	Jean	195·0-196·8	Lewkowitsch	73·7-73·9	Lewkowitsch	38	Jean
	0·9270	Amthor and Zink			90·3	Amthor and Zink		

Physical and Chemical Constants of the Mixed Fatty Acids.

Solidifying Point. Titer Test.	
°C.	Observer.
27·1-28·6	Lewkowitsch

NEAT'S FOOT OIL

French—*Huile de pieds de bœuf.* German—*Ochsenklauenoel, Rinderklauenoel.* Italian—*Olio di piede di bove.*

For tables of constants see pp. 688, 689.

Neat's foot oil is the oil obtained from the feet of cattle by boiling with water. It is a pale yellow, odourless oil, of bland taste. On standing the oil deposits "stearine." The glycerides contained in neat's foot oil consist of palmitin, stearin, and olein. Linolin appears to be absent, for *Coste* and *Shelbourn* found amongst the oxidation products of the liquid acids of neat's foot oil dihydroxystearic acid only. The amount of unsaponifiable matter varies from 0·12 to 0·65 per cent.

Commercial samples, even if unsophisticated with foreign oils, consist mostly of true neat's foot oil mixed with sheep's foot and horses' foot oils.

The high price of the oil acts as an incentive to fraud. It is largely adulterated with vegetable oils, such as rape oil and cotton seed oil. Also fish oils and mineral oils are used for the same purpose. These adulterants can be easily detected by the determination of the iodine value. The presence of vegetable oils can be unmistakably ascertained by the phytosteryl acetate test, if the amount of vegetable oils added be so small that the indications furnished by the iodine value of the sample, the iodine value of the liquid fatty acids, the saponification value (rape oil), and other chemical or physical tests, do not lead to decisive results.

Fish oils are best detected by the hexabromide test; mineral oil is easily determined and identified by examining the "unsaponifiable" matter.

Neat's foot oil is a valuable lubricating oil. A specimen of true neat's foot oil required in *Redwood's* Viscosimeter at 140° F., 70 seconds; and at 200° F., 43 seconds. It is also used in the leather industry (*Parker*[1]).

Lard Oil (see under "Lard").

Tallow Oil (see under "Tallow").

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[1] *Journ. Soc. Chem. Ind.* 1898, 5.

[Table

Physical and Chemical Constants of Neat's Foot Oil

Specific Gravity.			Solidifying Point.		Saponification Value.		Iodine Value.	
At °C.		Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
15	0·914-0·916	Allen	0 to 1·5	Schaedler	194·3[2]	Lewkowitsch	69·3-70·4[2]	Lewkowitsch
15	0·9152-0·9165[1]	Jean	10[1]	Jean	195·5-197·4[3]	Coste and Parry	71·1-72·4[3]	Coste and Parry
15·5 (water at 15·5=1)	0·9169-0·9174[3]	Coste and Parry			196-199[5]	Holde and Stange	66-76[5]	Holde and Stange
15·5	0·9164[4]	Coste and Shelbourn					67·1-72·9[1]	Gill and Rowe
18	0·9142	Stilurell						
99 (water at 15·5=1)	0·8619	Allen						

Physical and Chemical Constants of Neat's Foot Oil—continued

<table>
<tr><th colspan="2">Reichert-Meissl Value.</th><th colspan="2">Hehner Value.</th><th colspan="2">Maumené Test.</th><th colspan="3">Refractive Index.</th></tr>
<tr><th>cc. 1/10 norm. KOH.</th><th>Observer.</th><th>Per cent.</th><th>Observer.</th><th>°C.</th><th>Observer.</th><th colspan="2">At 20° C.</th><th>Observer.</th></tr>
<tr><td rowspan="7">1·0[4]</td><td rowspan="7">Coste and Shelbourn</td><td rowspan="7">95·3-95·5[3]
95·2[4]</td><td rowspan="7">Coste and Parry
Coste and Shelbourn</td><td>47-48·5
42·2-49·5[1]
56-58[3]</td><td>Jean
Gill and Rowe
Coste and Parry</td><td colspan="2">1·4681[4]</td><td>Coste and Shelbourn</td></tr>
<tr><td colspan="2">Specific Temperature Reaction.</td><td colspan="3">Oleo-refractometer.</td></tr>
<tr><td>°C.</td><td>Observer.</td><td colspan="2">"Degrees."</td><td>Observer.</td></tr>
<tr><td rowspan="4">87·9-103·1[1]</td><td rowspan="4">Gill and Rowe</td><td colspan="2">−3 to −4
−1 to −3
at 22° C.</td><td>Jean
Pearmain</td></tr>
<tr><td colspan="3">Butyro-refractometer.</td></tr>
<tr><td>°C.</td><td>"Degrees."</td><td>Observer.</td></tr>
<tr><td>20</td><td>64·2[4]</td><td>Coste and Shelbourn</td></tr>
</table>

[1] American oil.

[2] Oil rendered in the laboratory.

[3] Two specimens of oil rendered in the laboratory.

[4] Average of samples rendered in the laboratory.

[5] Means of eleven samples of pure oil.

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.		Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.	
At 100° C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
0·8742-0·8800 [3] (water at 100° C. = 1)	Coste and Parry	26·1	Coste and Parry	29·8-30·8 [1]	Jean	200·6 201·2	Coste and Parry	61·98-63·26 [1]	Jean
		Titer Test.		28·5-29·2 [3]	Coste and Parry	202·9-206·3	Coste and Shelbourn	74·5-75·8	Coste and Parry
0·8713-0·8749 [4]	Coste and Shelbourn	26·1-26·5 [2]	Lewkowitsch					71·0-77 63·6-69·5	Coste and Shelbourn
		16-26·5 [1]	Gill and Rowe						

[1] American oil.

[2] Oil rendered in the laboratory.

[3] Two specimens of oil rendered in the laboratory.

[4] Average of samples rendered in the laboratory.

[5] Means of eleven samples of pure oil.

EGG OIL

French—*Huile des Jaunes d'Œufs.* German—*Eieroel.*
Italian—*Olio di uovo.*

For table of constants see p. 691.

Egg oil is prepared from the yolk of hard-boiled hen's eggs either by pressure or by solvents. *Paladino* and *Toso*[1] obtained by the former method 25 to 35 per cent, *Kitt*,[2] using ether as a solvent, 19 per cent only. Ether extracts, besides egg oil, other substances, notably lecithin.

The expressed oil has a yellow colour. The extracted oil, freed by filtration from other ether-soluble substances, was semi-solid and of an orange-yellow colour. The specimen examined by *Kitt* contained 0·2 per cent of lecithin, and 1·5 per cent of cholesterol; its acid value was 1·2.

Egg oil gives the elaïdin reaction. The acetyl value 11·9 recorded by *Kitt* does not necessarily point to the presence of hydroxylated fatty acids since even if the number itself were not open to doubt (cp. 274), the high amount of cholesterol in the oil conditions a notable acetyl value.

In the commercial determination of the fatty oil in the yolk, the choice of the solvent is by no means irrelevant. Thus *Jean*[3] has shown that by extracting one and the same specimen of dried yolk with the following solvents, petroleum ether, ether, carbon bisulphide, carbon tetrachloride, and chloroform, the following respective proportions of oil were obtained :—48·24 per cent, 50·83 per cent, 50·45 per cent, 50·30 per cent, and 57·66 per cent. In another specimen the yolk was extracted with three solvents successively ; thus petroleum ether extracted 27·3 per cent of oil ; the extract with ether then yielded 1·05 per cent; the subsequent extraction with chloroform yielded 1·37 per cent.

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[1] *Analyst*, 1896, 161.

[2] *Chem. Zeit.* 1897, 303.

[3] *Zeit. f. Unters. d. Nahrungs. und Genussm.* 1904, 232.

[TABLE

Physical and Chemical Constants of Egg Oil

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Hehner Value.		Refractive Index.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm KOH.	Observer.	Per cent.	Observer.	At 25° C.	Observer.
15	0·9144	Kitt	8-10	Paladino and Toso[1]	22-25	Paladino and Toso	190·2	Kitt	72·1	Kitt	0·4	Kitt	95·16	Kitt	1·4713	Spaeth
20	0·9156	Paladino and Toso					185·2-186·7	Paladino and Toso	81·2-81·6	Paladino and Toso	0·66	Spaeth			Butyro-refractometer.	
100 (water at 15° = 1)	0·881	Spaeth					184·4	Spaeth	68·5	Spaeth					At 25° C.	Observer.
															68·5	Spaeth

Physical and Chemical Constants of the Mixed Fatty Acids

Melting Point.		Neutralisation Value.		Iodine Value.		Mean Molecular Weight.	
°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.		Observer.
34·5-35	Paladino and Toso	194·9	Kitt	72·6	Spaeth	285	Kitt
36	Spaeth			73·25	Kitt		
36-39[2]	Kitt						

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[1] *Analyst*, 1896, 161.

[2] Capillary tube method.

II. SOLID FATS

1. Vegetable Fats

The members belonging to this class are solid in temperate climates. They present, however, a variety of gradations from the soft, buttery mass of laurel oil to the hard, wax-like Japan tallow. As the hardness of the fats increases approximately in direct proportion to the decrease of glycerides of oleic acid and linolic acid, the iodine value seems most apt to determine, in the absence of other chemical characteristics, the order in which the individual fats should be enumerated. Palm nut oil and cocoa nut oil, however, have been placed together as undoubtedly constituting, together with mocaya oil, maripa fat, and similar fats, a well-defined group, differing from all other vegetable fats by a considerable amount of glycerides of lower fatty acids; in this respect they resemble to some extent butter fat.

PONGAM OIL[1]

This oil is obtained from Pongam beans, the fruits of *Pongamia glabra*, Vent. (*Dahlbergia arborea*, Roxb.[2]), a tall tree growing all over East India from the Central and Eastern Himalayas to Ceylon and Malacca.

The oil is known under the following native names:—Kanoogamanoo, Kanoogoo, Kanuga-Karra, Kanuga-Chettu, Kanugoo; it is also known as Korung oil and Kagoo oil.

According to *Lépine* (*Pharm. Journ.* (3) xl. 16) the seeds yield 27 per cent of a yellow oil, of the specific gravity 0·945, solidifying at 8° C. The authors of the *Pharmacographia Indica* state (see Watt's *Dictionary of the Economic Products of India*, VI. i. p. 322): "The oil which we have examined (called Houge oil in Mysore) and expressed purposely from fresh seeds was thick, of a light orange brown colour, and bitter taste. The specific gravity at 18° C. was 0·9458. It yielded 93·3 per cent fatty acids melting at about 30° C. . . . The bitter principle of the oil appears to reside in a resin, and not an alkaloid."

By extracting Pongam beans with ether I obtained 33·7 per cent of a buttery mass of a dirty-yellowish colour. I was enabled to examine, side by side with the oil I extracted from the seeds, another specimen obtained from India. This specimen contained 0·5 per cent

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[1] Lewkowitsch, *Analyst*, 1903, 342.

[2] This must not be confounded with the seeds of *Dahlbergia sissoo*.

of free fatty acids (in terms of oleic), and 6·9 per cent of unsaponifiable matter. The sample prepared in my laboratory contained 3·05 per cent of free fatty acids, and 9·22 per cent of unsaponifiable matter.

The oil is used in India for illuminating and medicinal purposes. As it can be obtained in large quantities, it should find technical application in the soap and candle industries.

Physical and Chemical Constants of Pongam Oil

Specific Gravity at ° C.		Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Refractive Index. Butyro-refractometer, "Degrees" at 40° C.	Observer.
15 (water at 15°=1)	0·93693[1]					Lewkowitsch.
40 (water at 40°=1)	0·9240[1]	183·1[1]	89·4[1]	1·1[1]	70[1]	,,
,,	0·9352[2]	178[2]	94·0[2]		78[2]	,,

Melting Point of the Fatty Acids

° C.
44·4[2]

CHAULMOOGRA OIL, GYNOCARD OIL (*see* Appendix)

French—*Beurre de Chaulmougra.* German—*Gynocardiaoel, Chaulmugraoel.* Italian—*Olio di chaulmugra.*

Physical and Chemical Constants of Chaulmoogra Oil

Saponification Value.		Iodine Value.	
Mgrms. KOH.	Observer.	Per cent.	Observer.
204	Lewkowitsch	90·35-90·9	Lewkowitsch

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[1] Specimen obtained from India.
[2] Extracted in the laboratory with ether.

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Iodine Value.	
°C.	Observer.	Per cent.	Observer.
Titer Test.			
39·5-39·6	Lewkowitsch	86	Lewkowitsch

Chaulmoogra oil is a fat of buttery consistency obtained from the seeds of *Gynocardia Prainii.* The seeds yield 40 to 45 per cent of fat. *Desprez*[1] has shown that the seeds obtainable in commerce are not those of *Gynocardia odorata,* as was hitherto supposed. The commercial seeds are said to be adulterated chiefly with those of various species of *Hydnocarpus.*

According to *Lemarié,*[3] however, gynocard oil is obtained from the "krebao" seed of Camboja, the product of one or more species of the *Hydnocarpus* (Chinese name "ta-fung-tze"). It is sold in Hanoi for medicinal purposes under the name "dai-phong-tu."

The "krebao" seeds contain 50 to 52 per cent of oil; only 30 per cent are obtained by expression.

In the fresh state chaulmoogra oil is white, odourless, and tasteless; on keeping it acquires a light brown colour, and an odour resembling that of bird lime.

The chemical composition of the fat is unknown. The acid value of a sample examined in my laboratory was 37·4.

Commercial samples of chaulmoogra oil were found to be adulterated by *Hirschsohn*[2] with cocoa nut oil, palm oil, and vaseline. Cocoa nut oil is detected by a lower iodine value, a higher saponification value, and a higher titer test of the mixed fatty acids than the normal ones. Palm oil would be detected by a lower iodine value than the normal one. The presence of vaseline would be revealed by a high proportion of unsaponifiable matter.

In Indo-China and Siam chaulmoogra oil is employed for medicinal purposes (*see* Appendix).

LAUREL OIL

French—*Beurre de laurier.* German—*Lorbeerfett.*
Italian—*Burro di lauro.*

For tables of constants see p. 696.

Laurel oil[4] is obtained from the berries of the laurel-tree (*Laurus nobilis,* L.), either by pressing, or by boiling the pounded berries with

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[1] *Journ. Soc. Chem. Ind.* 1900, 1025.

[2] *Pharm. Centr.-Halle,* 44, 627.

[3] *Bull. Imper. Inst.* 1903, 209.

[4] Laurel oil must not be confounded with the oil from the seeds of *Calophyllum inophyllum* (see table facing p. 553), specific gravity, 0·9315 at 16° C.; saponification value, 196·4; melting point of insoluble fatty acids, 37·6° C.

Nor must laurel oil be confounded with Indian laurel oil (described p. 502), from the fruits of *Laurus indica.*

water. The berries contain from 24 to 26 per cent of fat. Laurel oil has a green colour. At the ordinary temperature it has a buttery consistence; its taste and aromatic odour are characteristic.

Laurel oil is completely soluble in boiling alcohol; on cooling, crystals of trilaurin separate. Trilaurin is stated to be the chief constituent of this oil, but judging from the high iodine value it must contain considerable quantities of olein. On distilling laurel oil in *vacuo*, *Krafft* obtained trilaurin in the distillate. *Allen* also found small quantities of volatile acids (acetic). A sample examined by the writer had the acid value 26·3.

Laurel oil is only used in veterinary practice. It is sometimes adulterated with other fats (lard) coloured green with copper salts. Lard is detected by the phytosteryl acetate test; copper, by incinerating the oil and examining the ash.

Physical and Chemical Constants of Laurel Oil

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Reichert Value.	
°C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.
15	0·93317	Cloëz	24	Villon	33-36	Villon	198·9	Allen	67·8	De Negri and Fabris	1·6	Allen
98·5 (water 15·5=1)	0·8806	Allen	25	De Negri and Fabris	32-34	De Negri and Fabris	197·5	De Negri and Fabris	80·4-80·5	Lewkowitsch		
							197·7-198·1	Lewkowitsch	75-78·4	Wijs		

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Iodine Value.	
°C.	Observer.	Per cent.	Observer.
Titer Test. 14·3-15·1	Lewkowitsch	81·6-82·0	Lewkowitsch

CARAPA OIL, CRAB WOOD OIL, ANDIROBA OIL

French—*Beurre (huile) de Carapa.* German—*Carapafett.*
Italian—*Olio di Carapa.*

For table of constants see p. 698.

This fat is expressed from the seeds of several species of plants belonging to the genus *Carapa*, as *Carapa guianensis*, *Carapa moluccensis.* The seeds contain 40 to 50 per cent of fat. The oil has a not unpleasant vegetable odour, and is characterised by an intensely bitter flavour.

A specimen from Trinidad examined by *Deering* had the acid value 22·6; the melting point of the mixed fatty acids was 38·9° C. (*Deering*), 56·4° C. (*Milliau*).

Carapa oil is expressed in Brazil, Guiana, the West Coast of Africa, India, the Moluccas, for the purposes of soap-making, etc.; it is also imported into this country and into France.

[TABLE

Physical and Chemical Constants of Carapa Oil

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Hehner Value.	
At ° C.		Observer.	° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.
15	0·912	Millian[1]	36	Hannau[3]	31	Hannau	195·6	Deering	72·1	Hannau	2·2[5]	Deering	93·7	Deering
15·5	0·9225	Deering[2]							65[4]	Deering			95·5	Milliau

[1] *Corps gras ind.* 1899, 129.

[2] *Journ. Soc. Chem. Ind.* 1898, 1156.

[3] *Annali del Laboratorio delle Gabelle*, 1891-1892, p. 271.

[4] Calculated by the writer from the bromine value 41.

[5] Calculated by the writer from Deering's analytical data; volatile fatty acids equivalent to 0·25 per cent KOH.

MARGOSA OIL[1]

(VEEPA OIL, VEPPAM FAT, NEEM OIL)

This oil is obtained from the seeds of *Melia azedarach* (*Azadirachta indica*, Juss.), a large tree 40 to 50 feet in height, common in its wild or more often cultivated state throughout the greater part of India and Burma.

The oil has been described somewhat fully in the *Pharm. Journ.* by *Warden* (see Watt's *Dictionary of the Economic Products of India*, vol. v. p. 211).

The specimen of fat examined by me was solid at the ordinary temperature.

Physical and Chemical Constants of Margosa Oil

Specific Gravity		Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Refractive Index. Butyro-refractometer at 40° C.	Observer.
At ° C.					"Degrees."	
16 (water at 16°=1)	0·91425	196·9	69·6	1·1	52	Lewkowitsch
40 (water at 40°=1)	0·9023					

Titer Test of the Fatty Acids

° C.
42·0

KADAM SEED FAT[2]

This fat is obtained from the seeds of *Hodgsonia* (*Trichosanthes*) *Kadam*, Miq., belonging to the *Cucurbitaceæ*, a climbing plant occurring in Padang (Sumatra).

Kadam seed fat is prepared by cutting the fruit into pieces, drying in the sun for a couple of days and then expressing in bags.

The fat has at the ordinary temperature the consistence of butter; is yellow, non-drying, and odourless.

It consists of 80 per cent of triolein and 20 per cent of tripalmitin.

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[1] Lewkowitsch, *Analyst*, 1903, 342.

[2] Sack, *De Indische Mercuur*, 1903, 28 (April).

Specific Gravity.		Melting Point.		Iodine Value.		Saponification Value.	
At 15° C.	Observer.	° C.	Observer.	Per cent.	Observer.	Mgrms. KOH.	Observer.
0·919	Sack	21	Sack	68·96[1]	Sack	197·6[2]	Niederstadt
				66[3]	Niederstadt		

MAHUA BUTTER, ILLIPÉ BUTTER

French—*Huile de Mahwah, Beurre d'Illipé.*
German—*Mahwahbutter, Illipéoel.* Italian—*Burro di Illipé.*

For tables of constants see p. 701.

Mahua butter is the fat obtained from the seeds of *Bassia latifolia*, and must not be confounded with Mowrah butter, as has been done by earlier writers, who were no doubt misled by the similarity of the name.[4] The seeds contain 50 to 55 per cent of fat.

In the solid state this oil has a yellow colour; in the melted state the tint varies from yellow to orange.

Crossley and *Le Sueur* have examined a number of genuine specimens, obtained from official sources in India, where this fat is largely used for edible purposes. The numbers are reproduced in the following table :—

No.	Origin.	Specific Gravity at 100° C. (Water 100° C. = 1.)	Melting Point, ° C.	Acid Value.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Hehner Value.	Butyro-refractometer.	Viscosity.	
										Seconds at 140° F.	Compared with water.
1	Bengal	0·8975	24·5	11·79	194·00	62·11	0·44	94·95	..	97·1	4·24
2	,, ...	0·8962	26·0	19·15	192·60	64·88	..	..	51·8	93·8	4·10
3	Madras	0·8981	25·0	10·33	191·80	67·85	..	..	..	96·9	4·23
4	,, ...	0·8970	26·5	4·83	190·90	58·53	..	..	..	107·0	4·67
5	,, ...	0·8964	29·0	8·67	187·40	58·45	..	94·69	..	100·6	4·39
6	North-West Provinces .	0·8969	23·0	21·20	189·50	63·51	..	..	..	93·9	4·10
7	Central Provinces . .	0·8971	24·0	17·05	188·80	63·01	..	..	..	96·7	4·22
8	Calcutta	0·8943	25·5	70·82	193·20	58·59	0·88	..	..	90·4	3·95
9	Bombay	0·8980	24·0	6·83	190·50	53·43	..	..	52·4	96·9	4·25

Blumenfeld and Seidel[5] ascertained in a specimen of illipe butter 1·43 per cent of volatile fatty acids.

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[1] Calculated by the writer from the numbers given in the original paper.

[2] Sack, *De Indische Mercuur*, 1903, 28, April.

[3] Fat obtained from Brazil.

[4] The fat from *Bassia butyracea* is the commercial *Phulwara Butter* (p. 721).

[5] *Mitth. d. k. k. technolog. Gewerbe Museums*, 10. 160.

Physical and Chemical Constants of Mahua Butter

Specific Gravity.		Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.	
At 100° C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
		19-22	De Negri and Fabris	28-31	De Negri and Fabris	190·9	De Negri and Fabris	60·4	De Negri and Fabris
(water 100° C. = 1) 0·8943-0·8981	Crossley and Le Sueur			23-29	Crossley and Le Sueur	187·4-194·0	Crossley and Le Sueur	53·43-67·85	Crossley and Le Sueur

Physical and Chemical Constants of Mahua Butter—continued

Reichert-Meissl Value.		Hehner Value.		Refractive Index.		Viscosity.	
cc. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	At 40° C.	Observer.	Seconds at 140° F.	Observer.
0·44-0·88	Crossley and Le Sueur	94·69-94·95	Crossley and Le Sueur	Butyro-refractometer.		90·4-107	Crossley and Le Sueur
				51·8-52·4	Crossley and Le Sueur		

MOWRAH SEED OIL,[1] MOWRAH BUTTER

French—*Huile de Mowrah.* German—*Mowrahbutter, Bassiaoel.*
Italian—*Burro di Mowrah.*

For tables of constants see p. 703.

Mowrah seed oil is obtained from the seeds of *Bassia longifolia.* The commercial fat is a mixture of Mowrah seed oil with Mahua butter or illipe butter, the fat from *Bassia latifolia* (cp. p. 700). The seeds contain 50 to 55 per cent of fat.

The following yields are obtained on a commercial scale from the brands named :—

Siack . . .	43 per cent.
Singapore . . .	43 ,,
Balan . . .	52 ,,
Pulghères . . .	32 ,,

In the fresh state the fat is yellow; on exposure to the air the colouring matter is bleached. Mowrah seed oil has a bitter aromatic taste and a characteristic odour recalling that of cacao beans. The commercial samples contain considerable quantities of free fatty acids; the crystals may be recognised under the microscope. Thus *Nördlinger* found in a sample 28·54 per cent of free fatty acids; samples examined in the writer's laboratory contained 17·2 to 20 per cent. The chief constituent of the solid fatty acids is palmitic acid. A specimen examined in the writer's laboratory contained 2·34 per cent of unsaponifiable matter.

Mowrah seed oil is an important article of commerce. In India it is employed for various technical purposes, and fills the place of tallow where religious tenets forbid the employment of the latter. Under the name *Me oil* it is applied externally in the treatment of skin diseases. Mowrah seed oil is largely imported from India into this country and into France; it is used for candle and soap making.

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[1] Valenta, *Dingl. Polyt. Journ.* 251. 461.

[TABLE

Physical and Chemical Constants of Mowrah Seed Oil

Specific Gravity.		Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Hehner Value.	
At 15° C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.
0·9175	Valenta	17·5-18·5	Valenta	25·3	Valenta	192·3	Valenta	50·1	De Negri and Fabris	1·66	Lewkowitsch	94·76	Valenta
		36	De Negri and Fabris	42	De Negri and Fabris	188·4	De Negri and Fabris	62[2]	Lewkowitsch				
						192·4[2]	Lewkowitsch	63·9[2]	,,				
						190·8[2]	,,						

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.
38	Valenta	39·5	Valenta	56·6[2]	Lewkowitsch
40	De Negri and Fabris	45	De Negri and Fabris		
39·7-40·3[2] (Titer)	Lewkowitsch				

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[1] Valenta, *Dingl. Polyt. Journ.* 251. 461.

[2] Commercial samples.

CHAMPACA FAT

This fat is obtained in the Dutch Indies from *Melia Champaca*. It is stated by *Sack*[1] to consist of 70 per cent of triolein, and 30 per cent of tripalmitin.

Physical and Chemical Constants of Champaca Fat

Specific Gravity.	Melting Point °C.	Iodine Value.
0·903	44-45	60·25[2]

SHEA BUTTER, GALAM BUTTER

French—*Beurre de Cé*, *Beurre de Shée*, *Suif de Noungou*.
German—*Sheabutter*, *Galambutter*. Italian—*Burro di Seha*.

For tables of constants see p. 705.

This fat is obtained from the seeds of *Bassia Parkii*, DC. (*Butyrospermum Parkii*); the seeds contain 49-52 per cent of fat. Shea butter is characterised by a grey or greyish-white colour and a peculiar aromatic odour. It is somewhat viscous, possessing, at the ordinary temperature, the consistence of butter.

Stohmann's[3] statement that shea butter consists of tristearin and triolein, in the proportion of seven parts of the former to three parts of the latter, is not borne out by the iodine value ascertained in the writer's laboratory. The sample examined in my laboratory had the acid value 29·43; its low saponification value points to the presence of a notable amount of unsaponifiable matter. The specimen examined by *Kassler*[4] had the acid value 9·16. *Stohmann* obtained 3·5 per cent of an unsaponifiable wax-like substance from a specimen examined by him. The considerable amount of unsaponifiable militates against shea butter being used for soap-making purposes.

Shea butter would seem to form a good raw material for candle-making provided the fatty acids crystallise readily. *Kassler* obtained by hydrolysing shea butter in an autoclave under a pressure of 9 atmospheres with 3 per cent of magnesia, 92 per cent of fatty acids of the solidifying point 48·4°. On distilling the fatty acids on a large scale, the samples taken from the condenser during the first twenty-four hours had solidifying points from 48·9° to 51·3°, and iodine values from 47·03 to 51·32. In the following six hours of the distillation process small amounts of hydrocarbons were formed, increasing from 0·34 per cent to 5·07 per cent (cp. chap. xvi.).

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[1] J. Sack, *Indische Mercuur*, 1903, April 28.

[2] Calculated by the writer from the percentage of olein.

[3] Muspratt's *Chemie*, 4th edition, vol. iii. p. 574.

[4] *Augsburger Seifensieder Zeitung*, 1902. 311.

Physical and Chemical Constants of Shea Butter

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Hehner Value.	
° C.		Observer.	° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	Per cent.	Observer.
15	0·9175	Valenta	17-18	Valenta	28	Allen	192·3	Valenta	56·2-56·9	Lewkowitsch	94·76	Valenta
,,	0·9177	Milliau			23-23·3	Stohmann	178·8	Lewkowitsch	67·2	Milliau		
98-99 (water 15·5=1)	0·859	Allen			25·3	Valenta	182·4	Kassler				

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.	
° C.	Observer.	° C.	Observer.	Per cent.	Observer.
38	Valenta	39·5	Valenta	56-57·2	Lewkowitsch
52·5	Milliau	56	Stohmann	55·6	Kassler
		56·5	Milliau		
Titer Test.					
53·75-53·8	Lewkowitsch				
48·6	Kassler				

PALM OIL

French—*Huile de palme.* German—*Palmoel.*
Italian—*Olio di palma.*

For tables of constants see pp. 707, 708.

Palm oil is obtained from the fleshy part of the fruit of the palm trees *Elæis guineensis* and *Elæis melanococca*, which form vast forests along the West Coast of Africa, extending between Cape Blanco and St. Paul de Loando. Until recently, the West Coast of Africa was the only supplier of palm oil. Latterly, palm oil is also exported from the Philippines.

The fleshy part of the fruit forms, according to the variety of the palm tree, 27-70 per cent of the total fruit, whilst the seeds, freed from the shells, form 9-25 per cent. *Fendler*[1] has recently examined four varieties of palm fruits, locally known under the names *De*, *De-de bakui*, *Se-de*, and *Afa-de.* The following are the results of his examination :—

The fleshy part of fruit contains—	1 De.	2 De-de bakui.	3 Se-de.	4 Afa-de.
	Per cent.	Per cent.	Per cent.	Per cent.
Oil	66·5	58·5	59·2	62·9
Moisture	5·3	5·7	6·9	5·6

Besides these four recognised varieties of palm trees, there exist in the Cameroons two other varieties, termed the small-fruited and large-fruited "Lisombe palm,"[2] which differ from the ordinary palm tree in that the shells enclosing the kernel are more brittle than those of the ordinary palm nuts. The following table gives some information as to the Lisombe varieties, contrasted with the ordinary palm fruit :—

Variety.	Pulp in whole fruit.	Palm Oil in whole fruit.	Palm Oil contained in pulp.	Kernel in whole fruit.	Palm-kernel Oil in whole fruit.	Oil contained in kernel.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Small-fruited Lisombe	71·0	32·66	46·0	9·54	4·91	49·2
Large-fruited Lisombe, ripe	71·0	44·44	62·5	12·5	6·15	48·9
Large-fruited Lisombe, unripe	64·5	40·35	60·5	17·27	8·5	49·2
Ordinary Palm . .	37·5	22·64	60·3	14·58	7·13	48·9

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[1] *Berichte d. d. pharm. Gesellsch.* 1903, 115.

[2] Preuss, *Der Tropenpflanzer.*

Physical and Chemical Constants of Palm Oil

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.	
° C.		Observer.	° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
15	0·9209-0·9245	Tate	38[1]	Fendler	From 27 to 42·5 according to age and origin of the oil.		202-202·5	Valenta	53	Tolman and Munson
18	0·946	Stilurell	39[2]	,,	42[1]	Fendler	196·3	Moore	56	Lewkowitsch
50 (water 15·5 = 1)	0·8930	Allen	37[3]	,,	43[2]	,,	201-202	Thoerner	53·38[1]	Fendler
98-99 (water 15·1 = 1)	0·8586	,,	31[4]	,,	41[3]	,,	205·52[1]	Fendler	53·18[2]	,,
					35[4]	,,	203·78[2]	,,	57·44[3]	,,
							201·9[3]	,,	55·68[4]	,,
							200·8[4]	,,		

Physical and Chemical Constants of Palm Oil—continued

Reichert-Meissl Value.		Hehner Value.		Refractive Index.	
c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	At 60° C.	Observer.
0·86[1]	Fendler	95·6	Hehner	1·4510	Thoerner
0·74[2]	,,	94·2-97	Tate		
1·87[3]	,,				
0·90[4]	,,				

[1] From De palm ; the oil contained 54·06 per cent free fatty acids (calculated to oleic).
From De-de bakui palm ; ,, ,, 55·07 ,, ,, ,,
[3] From Se-de palm ; ,, ,, 55·38 ,, ,, ,,
[4] From Afa-de palm ; ,, ,, 57·18 ,, ,, ,,

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.			Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.	
° C.		Observer.	° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.
98-99 (water 15·5 = 1)	0·8369	Allen	Average 44·13	De Schepper and Geitel	47·75	Valenta	206·5-207·3	Valenta	273	Tate	53·3	Thoerner
100 (water 100 = 1)	0·8701	Archbutt	As a rule 44·5-45 ; rarely 39-41 or 45·5-46·2		47·8	Hübl	204	Thoerner	270	Allen		
					50	Allen			263	Williams	Liquid Fatty Acids.	
			42·5-43	Valenta								
			42·7	Hübl							94·6	Lewkowitsch
			45·5	Allen							99	Tolman and Munson
			Highest 45·4-45·5	Lewkowitsch								
			Lowest 35·8-35·9	,,								

It may be pointed out that enormous quantities of palm oil are being lost in consequence of the exceedingly crude manner in which the oil is recovered by the natives. This is done either by storing the fruits for some time in holes in the ground, when fermentation of the mass sets in and the oil rises to the surface, or by expressing the oil from the fresh fruits by beating with wooden pestles or by pressing by hand. The former process yields the lower but "harder" qualities, whereas by the latter the finer and "softer" palm oils are obtained. The fruit kernels remain intact in either of these processes (see "Palm Nut Oil.")[1]

Palm oil has a somewhat sweetish taste; in its perfectly fresh state is a good edible fat, and is used as such in Africa even by Europeans. Its odour is pleasant and resembles that of violets; this odour is not destroyed by bleaching with air at higher temperatures, and persists even after the oil has been made into soap. In consequence of the very crude mode of manufacture, the palm oil remains in contact with fermentable vegetable tissue, and hydrolysis rapidly sets in, so that palm oil, when it reaches the coast, contains already a notable amount of free fatty acids. Palm oil on being shipped from the coast contains, therefore, at least 10-12 per cent of free fatty acids. The process of hydrolysis once begun, continues in the barrels during the voyage, and in consequence thereof commercial palm oils, on arriving at their destination, contain frequently from 20 to 50 and even more per cent of free fatty acids. The hydrolysis may in old samples even reach completion, so that such palm oil practically consists of free fatty acids (*Lewkowitsch*).

The following table, due to *Y. de Schepper* and *Geitel*,[2] gives the proportion of water, impurities, neutral fat, and the solidifying points of the mixed fatty acids of a number of commercial brands of palm oil:—

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[1] A proposal to crush fruit and kernels together so as to obtain a mixed oil (pulp oil and kernel oil) has recently been patented by *A. Hallet*, Fr. Pat. 321,918.

[2] *Dingl. Polyt. Journ.* 245, 295.

[TABLE

Kind of Oil.	Water.	Impurities.	Solidifying Point of Fatty Acids.	Neutral Fat.
	Per cent.	Per cent.	°C.	Per cent.
Congo	0·78-0·95	0·35-0·7	45·90	16-23·0
Saltpond[1]	3·5-12·5	0·9-1·7	46·20	15-25
Addah	4·21	0·35	44·15	18·0
Appam	3·60	0·596	45·0	25·0
Winnebah	6·73	1·375	45·6	20·0
Fernando Po	2·68	0·85	45·90	28
Brass	3·05	2·00	45·1	35·5
New Calabar	3·82	0·86	45·0	40·0
Niger	3·0	0·70	45·0	40·0-47·0
Accra	2·2-5·3	0·60	44·0	53-76
Benin	2·03	0·20	45·0	59-74
Bonny	3·0-6·5	1·2-3·1	44·5	44·0-88·5
Gr. Bassa	2·4-13·1	0·6-3	44·6	41-70·0
Cameroons	1·8-2·5	0·2-0·7	44·6	67-83
Cape Labon	3·6-6·5	0·7-1·5	41·0	55-69
Cape Palmas	9·7	2·70	42·10	67
Half Jack-Jack	1·9-4·2	0·7-1·24	39-41·3	55-77·0
Lagos	0·5-1·3	0·3-0·6	45·0	58-68
Loando	1·5-3·0	1·0-1·9	44·5	68-76
Old Calabar	1·3-1·6	0·3-0·8	44·5	76-83
Gold Coast	1·98	0·50	41·0	69
Sherboro	2·6-7·0	0·3-1·2	42·0	60-74
Gaboon	2·0-2·8	0·3-0·7	44·5	79-93·0

The consistence of commercial palm oil varies, from that of butter (Lagos oil) to that of tallow (Congo oil). Also the colour varies greatly, ranging, through all shades, from orange-yellow (Lagos) to dark dirty red (Congo).

The colouring matter of palm oil is not affected in the process of saponification by means of alkalis or lime; in the acid saponification process, however, the colouring matter is destroyed. The colouring matter is slowly destroyed on exposure to air, more rapidly on heating or by bleaching with chemicals. The two latter processes are adopted in practice for preparing bleached palm oil.

Since palm oil, as pointed out already, is bleached by mere exposure to the atmosphere, hydrogen peroxide contained in the atmosphere is assumed to be the bleaching agent. This finds support in the fact that *Schönbein* obtained with a specimen of palm oil a hydrogen peroxide reaction. This explanation has been further elaborated by *Engler*.[2]

Although palm oil may be bleached by means of ozone, yet several ozone processes examined by the writer have hitherto not proved commercially successful, as the colour "reverts" in the palm oils so bleached. Bleaching by means of hot air, or by passing air through the heated oil, is capable of producing a tolerably white palm oil. The bleaching is carried out by blowing a current of air in a finely divided stream through the mass of oil, kept at a temperature of

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[1] This is the cheapest hard oil; "Drewin" is the cheapest soft oil.

[2] *Berichte*, 1900, 1007.

150° C. Heating the oil to temperatures of 250° C. does not produce a better result. In these processes the characteristic odour of palm oil is not destroyed.

The bleaching process most in vogue, and giving the best results, is the bichromate process. The oil is freed from its gross impurities, and treated according to its quality with 1-3 per cent of potassium bichromate, and the requisite amount of hydrochloric acid. The dark "chrome" liquor is then carefully run off, and the oil is washed with water, at first with the assistance of a little mineral acid, until it is quite free from chromium and mineral acid.

Not all palm oils can be bleached successfully. Lagos and Old Calabar oils yield good results, but dirty red-coloured oils, such as Congo oil, have hitherto withstood all attempts to bleach them.

The chief constituents of palm oil are palmitin and olein. The solid fatty acids consist, according to *Nördlinger*,[1] of 98 per cent of palmitic acid, 1 per cent of stearic, and 1 per cent of a heptadecylic acid, $C_{17}H_{34}O_2$ (most likely identical with daturic acid, p. 93). Two specimens of palm oil, Bassa raw, and Lagos bleached, examined in my laboratory yielded 0·53 per cent and 0·72 per cent of stearic acid respectively. *Hazura* and *Grüssner* found among the liquid fatty acids small quantities of linolic acid, identified by the sativic acid yielded on oxidation. This is confirmed by the iodine values of the liquid fatty acids recorded in the table (p. 708).

Colour reactions proposed for the identification of palm oil are useless, and in any case unnecessary, since palm oil cannot easily be confounded with other fats or oils. It may, however, be stated that some specimens of palm oil—Lagos oil and Old Calabar oil—give with sulphuric acid a colour reaction similar to that obtained with cod liver oil in chloroformic solution, although the blue is much fainter; other specimens do not give this blue colour, but turn red at once.

Palm oil is, as a rule, not adulterated with other fats, and the commercial valuation embraces, therefore, the determination of water, of impurities (mostly sand, added fraudulently by negroes), and of the solidifying point. The proportion of water and sand together should not exceed 2 per cent; for any excess, allowance is usually made by the seller.

Palm oil is chiefly used in the soap and candle industries. In the latter industry it is valued *cæteris paribus* by its "titer." On account of its non-drying qualities palm oil is also employed in the tinplate industry, to preserve the surface of the heated iron sheet from oxidation until the moment of dipping into the bath of melted tin.

For the purposes of the tin industry "palm oil greases" are sold, consisting of palm oil adulterated with cotton seed oil and mineral oil of the spec. grav. 0·905.

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[1] *Journ. Soc. Chem. Ind.* 1892, 445.

AKEE OIL[1]

French—*Huile d'Akee.* German—*Akeeoel.* Italian—*Olio di akee.*

Akee oil is a yellow, buttery fat, stated to be obtained from the arillus of *Blighia sapida*, a tree indigenous in West Africa (Guinea Coast).

The fatty acids distil unchanged under a pressure of 13 m/m. at 220°-225° C. They consist approximately of 50 per cent oleic acid and 50 per cent of solid saturated acids. The acid value of the sample examined was 20·1.

The oil appears to be very similar to palm oil.

Physical and Chemical Constants of Akee Oil

Specific Gravity.	Solidifying Point.	Melting Point.	Saponific. Value.	Iodine Value.	Reichert-Meissl Value.	Hehner Value.
99°-100° (water 15·5 = 1)	°C.	°C.	Mgrms. KOH.	Per cent.	cc. $\frac{1}{10}$ norm. KOH.	Per cent.
0·857	20	25-35	194·6	49·1	0·9	93

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.	Solidifying Point.	Melting Point.	Saponification Value.	Iodine Value.
99°-100° (water 15·5 = 1)	°C.	°C.	Mgrms. KOH.	Per cent.
0·8365	40-38	42-46	207·7	58·4
				Liquid Fatty Acids.
				82·4

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[1] Garsed, *Pharmac. Journ.* 1900, 691.

MACASSAR OIL

French—*Huile de Macassar.* German—*Macassaroel.* Italian—*Olio di Macassar.*

For table of constants see p. 714.

Macassar oil is the fat from the seeds of *Schleicheria trijuga*, Willd.[1] The seeds consist of 40 per cent of shells and 60 per cent of kernels. The latter yield 70·5 per cent of fat.

The fat forms at the ordinary temperature a yellowish-white mass of buttery consistence. It consists chiefly of the glycerides of lauric, palmitic, arachidic, and oleic acids, and contains also small quantities of acetic and butyric acids. The specimens examined by *Wijs*[2] contained 45 per cent of solid and 55 per cent of liquid fatty acids. A very small proportion of hydrocyanic acid, from 0·03 to 0·05 per cent (*Wijs*), seems to be characteristic of macassar oil. A sample examined in the writer's laboratory had the acid value 35·43. Specimens examined by other observers had acid values varying from 6·2 to 19·2. The amount of unsaponifiable matter in the specimen examined by *Wijs* was 3·12 per cent.

Macassar oil—native name in Celebes, *Ketjatkil oil*; native name in India, *Kon oil*—is greatly valued in its home on account of its alleged medicinal properties.

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[1] The native name (in Celebes) of the seeds is Kusambi nuts; hence the alternative name *Cassambium spinosum*. Other botanical names of the plant are *Stadmannia sideroxylon*, Bl., and *Mellicocca trijuga*, Juss.

[2] *Zeits. f. phys. Chemie*, xxxi. (Jubelband) 255.

[TABLE

Physical and Chemical Constants of Macassar Oil

Specific Gravity.		Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Hehner Value.	
At 15° C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.
0·924	Itallie	10	Glenk	22	Itallie	230	Itallie	53	Itallie	9	Wijs	91·4	Itallie
				22[1]	Wijs	221·5	Lewkowitsch	48·3	Lewkowitsch			91·5	Wijs
						215·3	Wijs[2]	69·1	Roelofsen				
								55	Wijs				

[1] By Crossley and Le Sueur's method.

[2] By *cold* saponification.

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
Titer Test. 51·6-53·2	Lewkowitsch	54-55	Itallie	191·2-192	Wijs	49·7-50·7	Lewkowitsch
						Liquid Fatty Acids.	
						103·2	Wijs

SAWARRI FAT [1]

French—*Huile de noix de Souari.* German—*Sawaributter.*
Italian—*Burro di noci di Souari.*

Physical and Chemical Constants of Sawarri Fat

Specific Gravity at 40° C. (Water at 15° = 1)	Solidifying Point. °C.	Melting Point. °C.	Saponific. Value. Mgrms. KOH.	Iodine Value. Per cent.	Reichert Value. c.c. $\frac{1}{10}$ norm. KOH.	Hehner Value. Per cent.
0·8981	29-23·3	29·5-35·5	199·51	49·5	0·65	96·91

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point. °C.	Melting Point. °C.	Mean Molecular Weight.	Iodine Value. Per cent.
47-46	48·3-50	272·8	51·5

Sawarri fat is the fat contained in the nuts from *Caryocar tomentosum*, imported occasionally from South America into this country as "butter nuts." The seeds contain 60 per cent of fat. The fat is colourless, and possesses a pleasant nutty taste. The free fatty acids in the specimen examined amounted to 2·4 per cent, calculated as oleic acid.

The solid fatty acids consist chiefly of palmitic acid. The liquid fatty acids contain besides oleic acid—identified by its oxidation product, dihydroxystearic acid—a hydroxylated acid which is readily converted into lactone. The acetyl value of the liquid fatty acids was 14·03.

MAFURA TALLOW [2]

French—*Graisse de Mafouraire.* German—*Mafuratalg.*
Italian—*Sego di Mafura.*

For tables of constants see p. 717.

Mafura tallow is contained in the seeds of *Mafureira oleifera* (*Trichilia emetica*). The fruits are small brown nuts, covered with a thin brown shell, which is easily detachable by rubbing; about 1600

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[1] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1890, 844; *Proceed. Chem. Soc.* 1889, 69.
[2] De Negri and Fabris, *Annali del Laboratorio Chimico delle Gabelle*, 1891-92, 271.

nuts weigh one pound. The kernels amount to 88 per cent and the shells to 12 per cent of the whole nuts. On extracting the nuts with ether 61 per cent. of fat are obtained, whilst the kernels alone yield 68 per cent, and the shells alone 14 per cent.[1]

The fat has a yellowish colour; it is free from taste; its odour recalls that of cacao butter.

According to *Villon* it consists of 55 parts of olein and 45 parts of palmitin. The high melting point of the mixed fatty acids would seem to render this fat especially suitable for the manufacture of soaps and candles.

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[1] *Bull. Imper. Inst.* 1903, 27.

Physical and Chemical Constants of Mafura Tallow

	Solidifying Point.		Melting Point.		Saponific. Value.		Iodine Value.	
	°C.	Observer.	°C.	Observer.	Mgrms. KOH	Observer.	Per cent.	Observer.
I. Prepared in the Laboratory	33-25	De Negri and Fabris	35-41	De Negri and Fabris	200·08	De Negri and Fabris	44·85	De Negri and Fabris
II. Commercial	37-30	De Negri and Fabris	35·5-42	De Negri and Fabris	220·96	De Negri and Fabris	46·14	De Negri and Fabris
	36	Schaedler	42	Schaedler				

Physical and Chemical Constants of the Mixed Fatty Acids

	Solidifying Point.		Melting Point.		Iodine Value.	
	°C.	Observer.	°C.	Observer.	Per cent.	Observer.
I.	47-44	De Negri and Fabris	51-54	De Negri and Fabris	46·92	De Negri and Fabris
II.	48-44	De Negri and Fabris	52-55	De Negri and Fabris	48·19	De Negri and Fabris

NUTMEG BUTTER, MACE BUTTER

French—*Beurre de muscade.* German—*Muskatbutter.*
Italian—*Burro di noce moscata.*

For tables of constants see p. 720.

Nutmeg butter is obtained from the seeds of *Myristica officinalis* (s. *moschata*, s. *fragrans*) (Molucca). The seeds contain 38-40 per cent of fat. Nutmeg butter has the consistence of soft tallow, is of whitish colour, and has the strong taste and odour of nutmegs.

This fat varies considerably in its composition (see table below). It contains from 4 to 10 per cent of an ethereal oil (hence low saponification value); and consists of about 45 per cent of a solid fat—chiefly trimyristin—the rest being a liquid fat and free fatty acids.

Cold alcohol dissolves the liquid fat, the free acids, and the ethereal oil (unsaponifiable), leaving about 45 per cent. undissolved. The undissolved portion yields on crystallisation from ether pure trimyristin, melting point 55° C.

Boiling alcohol, ether, and chloroform dissolve nutmeg butter almost completely. The solubility in alcohol is no doubt due to the high percentage of free fatty acids contained in the commercial samples.

The following table contains a few characteristics ascertained by *Dieterich ;* the first five samples were prepared by extracting nutmegs with ether :—

No. of Sample.	Specific Gravity at 15° C.	Melting Point. °C.	Acid Value.	Saponification Value.	Iodine Value.	Solubility in Parts of Boiling Alcohol.
1	...	...	22·4	156·8	...	...
2	...	...	22·4	159·6	...	...
3	0·996	51	22·4	154·0	...	15
4	...	...	22·4	156·8	...	...
5	...	...	22·4	156·8	...	...
6	0·945	42	39·2	151·2	...	12
7	0·957	45	33·6	140·0	...	12
8	0·966	48	44·8	134·0	..	10
9	...	38·5-39	17·25	178·25	45·32	...
10	...	42	19·60	173·13	42·71	...
11	...	43	18·67	172·2	40·14	...
12	...	42·5-43	18·67	174·54	41·38	...
13	...	39	21·93	175·93	52·04	...
14	..	38·5-39	22·80	178·67	48·60	...

The results of an examination of commercial samples of nutmeg butter by *Spaeth* are the following :—

Origin.	Melting Point °C.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Refractive Index.
					Butyro-refractometer at 40° C.
Banda .	25-26	170-173	77·8-80·8	4·1-4·2	76-82
Bombay .	31-31·5	189·4-191·4	50·4-53·5	1-1·1	48-49
Menado .	25·5	169·1	76·9-77·3	...	74-74·5
Penang .	26	171·8-172·4	75·6-76·1	...	84·5-85
Macassar	25-25·5	171·8-172·4	75·6-76·1	...	78·5
Zanzibar .	25·5-26	169·9-170·5	76·2-77	...	77·5

The discrepancies in the iodine values suggest the explanation that they may be caused by varying quantities of ethereal oil. An experiment carried out in my laboratory has, however, not confirmed this view, for a sample of genuine nutmeg butter of the iodine value 59·3 showed, after having been freed from its ethereal oil in a current of steam, the iodine value 58·3.

Nutmeg butter is liable to be adulterated with the fats from other *Myristica* species. Adulterations with waxes or unsaponifiable (mineral) waxes can be easily detected.

In the East nutmeg butter is used for medicinal purposes.[1]

The fats from other species of *Myristica* are related to nutmeg butter. The following fats from other *Myristica* species have been described :—

1. The fat from *Myristica ocuba*, commercially known as ocuba wax.
2. The fat from *Myristica otoba*, commercially known as otoba fat or otoba wax.
3. The fat obtained from *Myristica becuhyba*, known as ucuhuba fat, p. 733.
4. The fat from *Virola sebifera*, Aubl., obtained by boiling the fruit with water. It forms a yellowish tallow-like mass, of slight ethereal odour, having the specific gravity 0·995 at 15° C., and melting at 45° C. This fat is stated to consist chiefly of myristin and olein, and is used commercially in soap and candle making.
5. *Virola fat*, from *Virola venezuelensis*. The seeds, known in Venezuela by the local name "cuajo" contain, besides the fatty oil, an ethereal oil like the seeds from *Myristica moschata*. The seeds yield 47·5 per cent of a brown fat, from which pure myristin of the melting point 54°-55° C. can be obtained by crystallising twice from ether (cp. p. 91).
6. The fat from *Myristica argentea*.

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[1] Krasser, *Chem. Revue*, 1897, 331.

Physical and Chemical Constants of Nutmeg Butter

Specific Gravity.			Solidifying Point.		Melting Point.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.
15	0·945-0·996	Dieterich	41-42	Rüdorff	47-48	Rüdorff
98-99 (water 15·5=1)	0·898	Allen	Turbid at 33 rising to 41·5-44	Wimmel	43·5-44	Wimmel
					51	Dieterich
					42	,,
					45	,,
					48	,,
					38·5-43	,,

Physical and Chemical Constants of Nutmeg Butter—continued

Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Refractive Index.	
Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	$(n)_D$ at 40° C.	Observer.
154-159·6	Dieterich	40·1-52·0	Dieterich	1-4·2	Spaeth	1·4704	Utz
153·53-161	,,	59·3	Lewkowitsch			Butyro-refractometer at 40° C.	
169·1-191·4	Spaeth	50·4-80·8	Spaeth			67·0	Utz
		48·8-65·1[1]	Wijs				
		50·1-85·7[2]	,,				

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.	
°C.	Observer	°C.	Observer
40	Hübl	42·5	Hübl
Titer Test.			
35·5-35·95	Lewkowitsch		

[1] Oils expressed in Europe.

[2] Indian oils.

PHULWARA BUTTER, INDIAN BUTTER

French—*Beurre de Fulware.* German—*Fulwabutter, Phulwarabutter.*

This fat is expressed from the seeds of *Bassia butyracea,* the Indian "butter tree" indigenous in the Himalayas. It must not be confounded with Mowrah seed oil nor Mahua butter, the fats from *Bassia longifolia* and *Bassia latifolia* respectively. The seeds contain 50-52 per cent of fat, which is known commercially under the name "kariti" or "karité."

The specimen examined by *Crossley* and *Le Sueur* had the acid value 16·44.

Physical and Chemical Constants of Phulwara Butter

Specific Gravity. at 100° C. (Water 100°=1.)	Melting Point.	Saponific. Value.	Iodine Value.	Reichert-Meissl Value.	Hehner Value.	Refractive Index at 40° C.	Viscosity Seconds at 140° F.
	°C.	Mgrms. KOH.	Per cent.	c.c. $\frac{1}{10}$ norm. KOH.	Per cent.	Butyro-refractometer.	
0·8970	39	190·8	42·12	0·44	94·86	48·2	110·4

MKÁNYI FAT

French—*Suif de Mkany.* German—*Mkányifett.*
Italian—*Sego di Mkany.*

For tables of constants see p. 722.

This fat forms about 67 per cent of the seeds of *Stearodendron Stuhlmanni,* Engl., an East African *Guttifera* (called Mkányi by the natives of Uluguru).

The fat as prepared by the natives and marketed at Bogamoyo, is of yellowish-white colour. The acid values of various specimens of the native product were 23·33 (*Heise*); 11·6-20·7 (*Henriques*). According to *Heise,*[1] who first examined this fat, Mkányi fat consists chiefly of the mixed glyceride oleodistearin (p. 16), no palmitic acid having been found.

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[1] Heise, *Arbeiten aus dem kaiserlichen Gesundheitsamte,* 1896, 540.

[TABLE

Physical and Chemical Constants of Mkányi Fat

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Hehner Value.	
At C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.
15	0·9298	Henriques and Künne	38 at 39 crystals appear; remains liquid to 29·5, rising on solidifying to 36°.	Heise Henriques	40-41 completely melted at 42.	Heise Henriques	190·5 186·6-191·7	Heise Henriques	41·9	Heise	1·21	Heise	95·65	Heise
40	0·8926	Heise												
98 (water 15° = 1)	0·85606	,,												
100	0·8606	Henriques												

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.
57·5	Heise	59	Heise	42·1	Henriques
61·4-61·6 (Titer test)	Henriques	61·5	Henriques		

RAMBUTAN TALLOW[1]

French—*Suif de Rambutan.* German—*Rambutantalg.* Italian—*Sego di Rambutan.*

Rambutan tallow is obtained from the seeds of *Nephelinm Lappaceum*, indigenous to China and the Sunda islands. The seeds contain 40-48 per cent of fat.

Physical and Chemical Constants of Rambutan Tallow

Specific Gravity.	Solidifying Point.	Melting Point.	Saponific. Value.	Iodine Value.
	°C.	°C.		
0·9236	38-39	42-46	193·8	39·4

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.	Melting Point.	Neutralisation Value.	Mean Molecular Weight.	Iodine Value.
°C.	°C.			
57	58-61	186·4	300·9	41·0

The high mean molecular weight of the mixed fatty acids indicates the presence of fatty acids higher than stearic acid; indeed, arachidic acid was isolated. A small quantity of stearic acid was obtained; palmitic acid is stated to be absent. The proportion of oleic acid in the mixed fatty acids was found to be 45·5 per cent.

MALABAR TALLOW, PINEY TALLOW,[2] WHITE DAMMAR OF SOUTH INDIA

French—*Suif de Piney.* German—*Malabartalg, Vateriafett, Pineytalg, Pflanzentalg.* Italian—*Sego di Piney.*

For tables of constants see p. 724.

This fat is obtained from the seeds of *Vateria indica*, a tree indigenous to the East Indies. The fat is extracted by grinding the roasted seed and boiling the meal with water. The melted fat rises to the top and is skimmed off.

Malabar tallow is free from taste and odour. In the fresh state it has a greenish-yellow colour; on exposure to the air it is rapidly bleached. Its consistence approaches that of mutton tallow. The commercial fat contains about 2 per cent of a volatile oil of a pleasant odour, which can be extracted by alcohol. Two samples of fat examined by *Crossley* and *Le Sueur*[3] had the acid values 5·18 and 15·34 respectively.

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[1] Baczewski, *Journ. Soc. Chem. Ind.* 1895, 1049.

[2] Wagner's *Jahresbericht*, 1884, 1186.

[3] *Journ. Soc. Chem. Ind.* 1899, 991.

Physical and Chemical Constants of Malabar Tallow

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Viscosity.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per Cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Seconds at 140° F.	Observer.
9·4	0·9102	Dal Sie	30·5	Vierthaler and Bottura	36·5	Vierthaler and Bottura	191·9	Höhnel and Wolfbauer	37·82-39·63	Crossley and Le Sueur	0·22-0·44	Crossley and Le Sueur	101·5-104	Crossley and Le Sueur
15	0·915	Höhnel and Wolfbauer			30 42	Dal Sie Höhnel and Wolfbauer	188·7-189·3	Crossley and Le Sueur						
100 water at 100=1	0·8900-0·8907	Crossley and Le Sueur			37-37·5	Crossley and Le Sueur								

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.	
°C.	Observer.	°C.	Observer.
54·8	Höhnel and Wolfbauer	56·6	Höhner and Wolfbauer

The specimen of Malabar tallow examined by *Höhnel* and *Wolfbauer* consisted of 19 per cent of free fatty acids and 81 per cent of glycerides. The solid fatty acids melted at 63·8° C.

In India Malabar tallow is used as an edible fat.

CACAO[1] BUTTER

French—*Beurre de cacao.* German—*Kakaobutter.* Italian—*Burro di cacao.*

For table of constants see pp. 727, 728.

Cacao butter is expressed from the cacao beans, the seeds of the cacao-tree, *Theobroma Cacao.* The proportion of fat in the beans varies from 36·8 per cent to 50·9 per cent. (See Appendix.)

In determining the proportion of fat in the beans great care must be exercised in disintegrating the beans. It will be found best to preliminarily extract the bulk of the fats from the finely-divided mass, then to dry, grind up with sand, and exhaust completely. (See Appendix.)

On a large scale the cacao beans are roasted, ground, and the bulk of the fat is removed by hot expression in hydraulic presses. Before the ground material is put into the presses alkali carbonates are added; some manufacturers also add the carbonates before roasting. As the alkali will combine with any free fatty acids the manufactured product is practically free from fatty acids. Soaps are thus likely to pass into the expressed fat. Hence in the examination of cacao butter the ash should be determined.

Cacao butter has a yellowish-white colour, turning white on keeping. It possesses an agreeable taste and pleasant odour like chocolate. At the ordinary temperature it is somewhat brittle.

Amongst the solid cacao butter fatty acids, stearic, palmitic, and arachidic acids have been ascertained. The occurrence of lauric acid is doubtful (cp. *Traub*[2]). Theobromic acid $C_{64}H_{128}CO_2$ stated by *Kingzett*[3] to occur in the fat is, according to *Graf*,[4] most likely arachidic acid. Stearic acid occurs to an extent of 39 (*Lewkowitsch*[5]), to 40 per cent (*Hehner* and *Mitchell*[6]). *Farnsteiner* obtained by the barium salt benzene method 59·7 per cent of solid acids, 31·2 per cent of oleic acid, and 6·3 per cent of other liquid acids. Linolic acid has been proved to occur in cacao butter by *Benedikt and Hazura.*[7] The statement that cacao butter contains formic, acetic, and butyric acids (which was supported by a high Reichert value recorded in the literature), is erroneous.

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[1] I prefer the spelling "cacao" to "cocoa," in order to avoid the confounding of this fat with cocoa nut oil or kokum butter.

[2] Wagner's *Jahresbericht*, 1883, 1159.

[3] *Journ. Chem. Soc.* 1878, 38.

[4] *Arch. Pharm.* 1888, 830.

[5] Unpublished observations.

[6] *Analyst*, 1896, 328.

[7] *Monatshefte*, 1889, 353.

Klimont obtained from cacao butter oleopalmitostearin (see p. 15). *Fritzweiler*[1] isolated about 6 per cent of oleodistearin (p. 16).

In the pharmaceutical literature the statement was frequently made, and is still being copied into text-books, that cacao butter does not turn rancid. *Dieterich* contradicted this statement some years ago; I have then shown by an extended series of observations[2] that cacao butter does turn rancid like any other fat under conditions favouring hydrolysis and subsequent rancidity. I have proved this in a somewhat exaggerated manner by exposing fresh cacao butters to the atmosphere in sunlight, when rancidity set in in a few days (three to four days). It must be left undecided whether the older erroneous statements, based on somewhat limited experience, be due to the fact that cacao butter, owing to its high price, is being kept in a more careful manner than ordinary fats, or whether it be due to the aromatic principle of cacao butter preventing the setting in of hydrolysis (much as lard is preserved by "benzoating," *i.e.* by suspending powdered benzoin in the melted fat and allowing it to stand for some time).

The statement that rancid cacao butter is obtained from mouldy beans is erroneous, for most shipments of cacao beans become mouldy in transit. Since the beans in the first stage of manufacture are roasted the mould is destroyed, so that cacao butter prepared from mouldy beans need not of necessity become rancid.

The acid value of commercial samples of cacao butter was found by *Dieterich* from 1·0 to 2·3. *Lewkowitsch* found in a large number of genuine fresh cacao butters acid values varying from 1·1 to 1·95. A sample that had been kept ten years in a sealed bottle had the acid value 4·6.

On account of its high price cacao butter is frequently adulterated and also wholly substituted by chocolate fats. The latter consist chiefly of the "stearine" of cocoa nut and palm nut oils. They are readily differentiated from cacao butter by their Reichert-Meissl values, and especially their low iodine values.

Less decisive are the indications furnished by the melting point of the fat itself; in this connection it should be noted that the freshly melted cacao butter shows a considerably lower melting point than the normal one, and only regains its normal (higher) melting point when the sample has been kept for several days (in a desiccator). When determining the melting point it is best to proceed as described in Chapter V.[3]

For the detection of "chocolate fats" (sold under various fancy names, see chap. xv.), in genuine cacao butter the determination of the saponification value and the iodine value will as a rule suffice. These substitutes considerably raise the saponification value, whilst they lower the iodine value. Also the "titer" test of the fatty acids is considerably depressed by them. As a confirmatory test the determination of stearic acid may be carried out.

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[1] *Arbeiten aus dem kaiserlichen Gesundheitsamte*, 1902, 371.

[2] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1899, 557.

[3] Cp. also Welmans, "Ueber Oleum Cacao," *Pharm. Zeit.* 1900, 99.

Physical and Chemical Constants of Cacao Butter

Specific Gravity.[6]			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Hehner Value.		Refractive Index.		
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	At °C		Observer.
15	0·950-0·952	Hager	25-26	Herbst	32-34	Hager	192-202	Filsinger.	34	Hübl	0·2[1]	Lewko-witsch	94·59	Bensemann	60	1·4496	Thoerner
,,	0·964-0·976	Dieterich	27·3	Rüdorff	21-33·6	Filsinger	193·55	De Negri and Fabris	34-37·5	Filsinger					40	1·4565 to 1·4578[5]	Strohl
50 (water 15·5=1)	0·8920	Allen	23-21·5	De Negri and Fabris	30-32	Dieterich			36·62	De Negri and Fabris	0·5[2]	,,					
					30-34	,,	198-200	Thoerner			0·33-0·38[3]	,,					
			23	Thoerner	33·5	Rüdorff	191·8-194·5	Lewko-witsch	32·8-41·7[5]	Strohl							
98 (water 15·5=1)	0·8577	,,			28-30	De Negri and Fabris			34·3-37	Lewko-witsch	0·83[4]	,,					
					32-33	Thoerner											
					28-33	Lewko-witsch											
															Butyro-refractometer.		
															At 40° C.		Observer.
															46-47·8		Strohl
															46-46·5		Mansfeld

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[1] Genuine cacao butter, kept ten years in a sealed bottle.
[2] Prepared in the laboratory from nibs.
[3] Genuine English cacao butters, fresh.
[4] Genuine Dutch cacao butter, fresh.
[5] Forty commercial samples.
[6] According to *White* (*Pharm. Journ.* 1898, 69) the specific gravity of cacao butter when freshly melted rises gradually from 0·950 until it reaches its highest value 0·995 after a few days.

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.		Refractive Index.	
°C.	Observer.	°C.	Observer.	Mgrms KOH.	Observer.	Per cent.	Observer.	At 60° C.	Observer.
51	Hübl	52	Hübl	190	Thoerner	39·1	De Negri and Fabris	1·422	Thoerner
		48-49 51-52	Bensemann			32·6	Thoerner		
		49-50 52-53	,,						
47-45	De Negri and Fabris	48-50	De Negri and Fabris						
46-47	Thoerner	49-50	Thoerner						
Titer Test.									
48·3	Lewkowitsch								
49·2	,,								

The presence of vegetable oils, such as *almond oil*, *arachis oil*, *sesamé oil*, *hazel nut oil*, would be in the first instance readily recognised by an increase in the iodine value, and the lowering of the solidifying and melting points of the mixed fatty acids.

Bees' wax and paraffin wax (stated to have been employed as adulterants) will hardly be used now, as they are too easily detected by the lowering of the saponification value, and the increase in the amount of unsaponifiable matter. The presence of bees' wax would also be indicated in the first instance by a high acid value of the sample. Cacao butters of comparatively high acid values owe their acidity (in the absence of adulterants) either to rancidity (ascertainable by the taste), or to admixture with fat which has been extracted from cacao bean shells. Very likely the cacao butters in which *Filsinger* found as much as 28 per cent of free fatty acids were cacao butters obtained from shells.

The most difficult adulterant to detect was, until recently, tallow. *Hager's* aniline test recommended for that purpose has been found by me useless, and I therefore omit its description.[1]

Björklund's ether test may be recommended as a preliminary test. It is carried out as follows:[2]—Place about 3 grms. of the sample in a test-tube, add twice the weight of ether, at the temperature of 18° C., close the test-tube with a cork, and effect solution, if possible, by shaking. The fat should dissolve to a clear solution. Then immerse the tube in water of 0° C., and note the number of minutes which the liquid requires to become milky, or to deposit white flocks, and observe the temperature at which the solution becomes again clear when removed from the water. The

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[1] See 2nd edition of this work, p. 529.

[2] *Zeit. analyt. Chemie*, 3. 233.

following table gives *Björklund's* observations made on pure cacao butter and on samples mixed with tallow :—

	Turbidity at 0° C. after Minutes.	Clear Solution at °C.
Pure cacao butter	10-15	19-20
Cacao butter + 5 per cent of beef tallow .	8	22
Cacao butter + 10 per cent of beef tallow .	7	25

I[1] found, however, that cacao butters containing as much as 10 per cent of tallow will dissolve in two parts of ether at 18° C., although requiring a little longer time than genuine cacao butter does. The chief indication to be relied upon is not, therefore, the number of minutes required for crystallisation—as the time will vary for different samples—but the characteristic way in which genuine cacao butter crystallises as compared with adulterated samples. In the former case tufts of distinct crystals appear at the bottom and the sides of the containing vessel, whereas five and more per cent of tallow are recognised by flocks separating from the cooled solution.

The modification of *Bjorklund's* test recommended by *Filsinger*, viz. to dissolve two grams of the sample in 6 c.c. of a mixture of 4 parts of ether and 1 part of alcohol, is scarcely an improvement, and cannot therefore be recommended.

A reliable test to detect the presence of tallow is the phytosteryl acetate test; the microscopic examination for the presence of cholesterol crystals will not furnish decisive information (*Lewkowitsch*).[1]

Cacao butter is a by-product in the manufacture of chocolate, and therefore obtainable in large quantities. It is used in the manufacture of lower class chocolates (which are loaded with an excess of fat, in confectionery) in pharmacy, and in the preparation of perfumes.

CHINESE VEGETABLE TALLOW

French—*Suif végétal de la Chine.* German—*Chinesischer Talg. Stillingiatalg, Vegetabilischer Talg.* Italian—*Sego di Stillingia.*

For table of constants see pp. 731-733.

Vegetable tallow is the hard fat which coats the seeds of the Chinese tallow-tree, *Stillingia sebifera* (*Croton sebiferum, Sapium sebi-*

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[1] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1899, 557.

ferum),[1] grown extensively in China and Indo-China. The fruit contains three oval seeds surrounded by a thick tallow-like mass. The seeds themselves contain a brownish yellow oil, which has been described already (p. 470) under the name of stillingia oil. *Tortelli* and *Ruggeri*, who prepared the solid fat and the oil from the seeds separately, obtained 22 per cent of vegetable tallow and 19·2 per cent of stillingia oil. According to *Lemarié* (Director of Agriculture, Annam), the seeds of *Sapium sebiferum*, known locally as "cây-sói," yield 60 per cent of shells and 31 per cent of kernels. The shells contain 29·5 per cent of a white, solid fat, the kernels 59·5 per cent of oil.

According to the process of manufacture employed, two products are obtained. One process has for its object the separate production of vegetable tallow and stillingia oil. In this process the seeds are placed into perforated cylinders and steamed, so that the fat melts and runs off. This product is sold under the Chinese name "pi-iéou," or "pi-yu." The seeds are then removed and crushed separately for the recovery of the stillingia oil (see p. 470).

In the second process the seeds, together with their coating of fat, are crushed, and a mixture of vegetable tallow and stillingia oil is thus obtained.

The product from the latter process is naturally much softer than the true vegetable tallow. It has a lower melting point, and a much higher iodine value than the pure vegetable tallow. This second quality is sold under the name "mou-iéou," and represents a mixture of "pi-yu" and "ting-yu" (see p. 470).

Samples of vegetable tallow which have been prepared in the laboratory by extracting the crushed fruit with solvents, contain therefore stillingia oil, and such numbers as were given by *De Negri* and *Fabris* for vegetable tallow extracted by them from the seeds by means of ether and carbon bisulphide do not represent true vegetable tallow. Hence I have omitted numbers referring to a mixture of vegetable tallow and stillingia oil. Nor have I recorded numbers observed for commercial products, which undoubtedly represent a mixture of the two kinds of fat in the fruits.

Crushed vegetable tallow, if free from stillingia oil, leaves no grease-spot on paper. The samples examined in my laboratory had acid values varying from 7·07 to 7·51. *De Negri* and *Fabris* found 2·4; *De Negri* and *Sburlati*,[2] 2·2; *Klimont*, 14·2; *Zay* and *Musciacco*, 22·5.

According to *Maskelyne*, vegetable tallow consists of palmitin and olein. A confirmation of this statement may be found in the fact that *Hehner* and *Mitchell*[3] obtained no stearic acid crystals from a specimen absorbing 22·87 per cent of iodine. This is further confirmed by *Klimont*,[4] who found in a commercial sample (of the iodine value 27·6) palmitic and oleic acids only.

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[1] *Bull. Imperial Institute*, 1903, 209.

[2] De Negri and Sburlati, *Journ. Soc. Chem. Ind.* 1897, 339.

[3] *Analyst*, 1896, 328.

[4] *Monatshefte f. Chemie*, 1903, 408.

Physical and Chemical Constants of Vegetable Tallow

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.
15	0·918	Thomson and Wood	26·7	Thomson and Wood	44·5	Thomson and Wood	200·3 [3]	Lewkowitsch
15	0·915	Lemarié [1]	24·2-26·2 [3]	Lewkowitsch	43-46 [3]	Lewkowitsch	179 [3]	De Negri and Fabris
50	0·915	Jules Jean [2]	34 [3]	De Negri and Fabris	44 [3]	De Negri and Fabris	203·6 [3]	Hobein
			35 [3]	Hobein	35	Lemarié [1]	203·3 [4]	,,
			32 [4]	,,	43-45	Hobein	199-202·2 [5]	De Negri & Sburlati
			27·2-31·1 [5]	De Negri & Sburlati	39-42	,,	203·5	Klimont
100 (water 15=1)	0·8600	Zay and Musciacco	37·7	Zay and Musciacco	36·5-44·1 [5]	De Negri & Sburlati	231	Zay and Musciacco
					58·2	Jules Jean		
					36·4	Klimont		
					52·5	Zay and Musciacco		

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[1] Mou-iéou oil.

[2] *Zeit. ang. Chem.* 1898, 250.

[3] Commercial sample.

[4] Prepared from the seeds by steaming.

[5] Ten samples of commercial fat; the lower melting fats no doubt consisted of mou-iéou oil.

Physical and Chemical Constants of Vegetable Tallow—continued

Iodine Value.		Reichert-Meissl Value.		Hehner Value.		Refractive Index.				
						Oleo-refractometer.		Butyro-refractometer.		
Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	"Degrees."	Observer.	At °C.	"Degrees."	Observer.
32·1-32·3 [1]	Lewkowitsch	0·69	Zay and Musciacco	93·45	Zay and Musciacco	– 23	Jules Jean	50	38	Zay and Musciacco
22·87	Hehner and Mitchell									
35·5 [1]	Hobein									
28·5 [2]	,,									
28·5-37·7 [3]	De Negri & Sburlati									
38·3	Jules Jean									
19·0	Zay and Musciacco									
27·6	Klimont									

[1] Commercial sample.

[2] Prepared from the seeds by steaming.

[3] Ten samples of commercial fat; the lower melting fats no doubt consisted of mou-iéou oil.

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
	Titer Test.						
52·1-53·5[1]	Lewkowitsch	56-57	Mayer	182·1[1]	De Negri and Fabris	34·2-34·3[1]	Lewkowitsch
42[1]	De Negri and Fabris	47[1]	De Negri and Fabris	207·9[1]	Hobein	47[1]	De Negri and Fabris
41[1]	Hobein	51[1]	Hobein	206·4[2]	,,	54·1-54·8	,,
40[2]	,,	49[2]	,,	202-208·5[3]	De Negri and Sburlati	38·1[1]	Hobein
45·2-47·9[3]	De Negri and Sburlati	53-56·9[3]	De Negri and Sburlati			29·2[2]	,,
56·4	Jules Jean	56·8	Jules Jean	240·1 (!)	Zay and Musciacco	30·3-39·5[3]	De Negri & Sburlati
						Liquid Fatty Acids.	
						97·04	Zay and Musciacco

[1] Commercial sample.
[2] Prepared from the seeds by steaming.
[3] Ten samples of commercial fat; the lower melting fats no doubt consisted of mou-iéou oil.

On repeatedly crystallising vegetable tallow from acetone (*Klimont*),[1] oleodipalmitin was obtained. In *Klimont's* opinion, vegetable tallow consists chiefly of oleodipalmitin, with smaller quantities of tripalmitin.

Zay and *Musciacco* state that the mean molecular weight of the soluble fatty acids is 231·4, and that they isolated volatile fatty acids of the molecular weight 132·8. The low molecular weight of the insoluble fatty acids would point to the presence of lauric acid. The number 231·4 stands therefore in need of confirmation.

KOKUM BUTTER, GOA BUTTER, MANGOSTEEN OIL

French—*Beurre de Cocum.* German—*Kokumbutter.*
Italian—*Sego di Kokum.*

For table of constants see p. 735.

This fat is obtained in the East Indies from the seeds of the Guttifera, *Garcinia indica, Choisy* (*Mangosteena indica*). The seeds contain 20-25 per cent of fat.

The acid constituents of kokum butter are oleic and stearic acids, with small quantities of (probably) lauric acid. According to *Heise*[2] this fat (like Mkányi fat) consists chiefly of oleodistearin. The specimen examined by *Heise* contained 10·5 per cent. of free fatty acids, and that tested by *Crossley* and *Le Sueur*[3] 7·1 per cent calculated as oleic acid.

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[1] *Monatshefte f. Chemie*, 1903, 408.

[2] *Arbeiten aus dem kaiserlichen Gesundheitsamte*, 1896, 13. 302.

[3] *Journ. Soc. Chem. Ind.* 1898, 991.

Physical and Chemical Constants of Kokum Butter

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Hehner Value.		Refractive Index.		
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	At °C.		Observer.
40 (water 15° = 1)	0·8952	Heise	33·3	Redwood	36·7	Redwood	191·3	Heise	33·1	Heise	1·54	Heise	95·59	Heise	25	1·4628[2]	Heise
98 (water 15° = 1)	0·8574	,,	27·5	Flückiger and Hanbury	42·5-45	Flückiger and Hanbury	186·8	Crossley and Le Sueur	34·2	Crossley and Le Sueur	0·11	Crossley and Le Sueur	94·59	Crossley and Le Sueur	40	1·4565[2]	Crossley and Le Sueur
100 (water 100° = 1)	0·8889	Crossley and Le Sueur	37·6-37·9	Heise[1]	41-42	Heise[1]											
					42	Crossley and Le Sueur											

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point. °C.	Melting Point. °C.	Mean Molecular Weight.	Observer.
59·4	60-61	282	Heise

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[1] The melting point varied according to whether the melted fat was allowed to solidify rapidly at 0° C., or kept at the ordinary temperature; in the former case the melting point was 32°-33° C., in the latter it rose to 40° C. after 24 hours' standing (cp. p. 9).

[2] Calculated from observations made with the butyro-refractometer.

BORNEO TALLOW[1] (TANGKAWANG FAT)

French—*Suif végétale de Borneo.* German—*Borneotalg.*
Italian—*Sego di Borneo.*

Borneo tallow is obtained from the kernels of a number of plants belonging to the family of *Dipterocarpus*, as *Shorea stenoptera*, *Shorea aptera*, *Hopea aspera*, *Isoptera Borneensis*, etc., indigenous to the Sunda Islands. The fruits yield from 40 to 50 per cent of fat.

According to *Lemarié*, the fat is prepared by the natives in the following manner :—The hard fruits are left for some time in a damp place until the shell breaks and the seeds begin to germinate. They are then dried in the sun, and the kernels are separated from the pericarp and placed in baskets of bamboo canes, which are suspended over pots of boiling water. When the kernels have become soft and pasty, they are placed in bags and pressed. The fat thus obtained is moulded in the internodes of bamboo stems, hence the commercial samples have a cylindrical shape.

The native name of Borneo tallow is Minjak Tangkawang (Tangkawang Fat). In the following table I give some characteristics of the fats from *Shorea aptera*, *Isoptera Borneensis* and of a sample of unknown origin :—

Physical and Chemical Constants of Borneo Tallow (Tangkawang Fat).

	Melting Point.	Saponification Value.	Hehner Value.	Iodine Value.	Observer.
	°C.	Mgrms. KOH.	Per Cent.	Per Cent.	
Shorea aptera . .	31	191·2	95·5	15[2]	Heim
Isoptera Borneensis .		192·2	95·3	16[3]	,,
			95·7	31[4]	Geitel

Physical and Chemical Constants of the Mixed Fatty Acids

	Solidifying Point. °C.	Melting Point. °C.	Mean Molecular Weight.	Observer.
Shorea aptera . .	51	55	268	Heim
Isoptera Borneensis .	51	55	256	,,
	53·5-54		283·7	Geitel

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[1] Geitel, *Journ. Soc. Chem. Ind.* 1888, 391.

[2] Calculated from Heim's statement that the sample contains 16·7 per cent of oleic acid.

[3] Calculated from Heim's statement that the sample contains 18 per cent of oleic acid.

[4] Calculated from Geitel's statement that the sample contains 34 per cent of oleic acid.

Borneo tallow has a light green colour, changing to yellow, and after prolonged exposure to the air to white. It resembles cacao butter in consistence at the ordinary temperature as also in taste. It has a crystalline granular structure, and is covered with fine white needles of stearic acid, the quantity of which amounted, in the case of the specimen examined by *Geitel*, to 9·5-10 per cent. This specimen commenced to melt at 35-36° C., and liquefied completely at 42° C. The solidifying point of the free fatty acids was 53·5°-54° C.; they consisted of 66 per cent of stearic and 34 per cent of oleic acids. The somewhat low solidifying point of the mixed fatty acids would seem to indicate presence of palmitic acid. The probable iodine value of the fat, calculated from the last given figure, is about 31. I therefore place Borneo tallow next to kokum butter.

Borneo tallow is employed by the natives for edible purposes; in Manila it is used for the manufacture of candles. It is exported to Europe and should prove a valuable material for soap and candle making.

DIKA BUTTER, DIKA OIL, OBA OIL, WILD MANGO OIL

French—*Beurre de Dika.* German—*Dikafett.* Italian—*Sego di Dika.*

Physical and Chemical Constants of Dika Oil

Specific Gravity.		Solidifying Point.		Melting Point.		Saponification Value.	Iodine Value.	
At °C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Per cent.	Observer.
0·820	Schaedler			30-31	Hamel-Roos	173·1 (?)	30·9-31·3	Dieterich
?				29	Dieterich			
		34·8	Heckel	41·6	Heckel			

This fat is obtained from the seed kernels of *Irvingia gabonensis*,[1] (*Irvingia Barteri*,[2] *Mangifera gabonensis*) indigenous to the West Coast of Africa. The tree is known by the natives of West Africa as the "udika," "dika," "dita," "oba," and "iba" tree. The seeds yield from 60-65 per cent of fat. This is obtained by the natives by boiling the seed kernels with water and expressing the oil.

The fresh dika butter is white, has a sweet odour, and an agreeable taste. On keeping it becomes orange-yellow; in the melted state it is yellowish-grey. The characteristic smell becomes more distinct on warming.

According to *Oudemans*,[3] this fat consists of laurin and myristin only, to the exclusion of olein. The same statement has been repeated by *Heckel*, on the ground that he could not obtain from the

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[1] Heckel, 2° *Mémoire des Annales du Musée et de l'Institut Colonial de Marseille.*

[2] *Bull. Imper. Inst.*, 1903, 207.

[3] *Journ. prakt. Chemie*, 81. 356.

fatty acids an ether-soluble lead salt. This, however, is not definite proof (p. 348). At any rate, it cannot hold good for the specimen examined by *Dieterich*, he having found 30·9-31·3 as the iodine value of the fat, corresponding to about 34 per cent of olein. The acid value of the specimen examined by *Dieterich* was 19·6. Dika butter is stated to behave in *Björklund's* ether test like cacao butter.

CAỸ-CAỸ FAT, COCHIN CHINA WAX, IRVINGIA BUTTER

German—*Cochinchina Wachs.*

The fat from *Irvingia Oliveri*, *Irvingia malayana*, or *Irvingia Harmadiana*, the Indo-Chinese wax- or candle-tree (indigenous to Cochin China), is, according to *Heckel*, almost identical with Dika butter. The seed kernels contain from 52-56 per cent of fat, which is extracted by the natives in a primitive fashion. The crude fat is sold under the name of Caỹ-Caỹ wax. It is of a greenish-yellow colour, becoming white on exposure to the air. The fat melts at 38° C. and solidifies at 35° C. *Vignoli's* statement that Caỹ-Caỹ wax contains 70 per cent of saturated fatty acids (?), 30 per cent of which are oleic acid, requires confirmation.

The best qualities of Caỹ-Caỹ fat are used as an edible fat in place of butter. In Cambodja the fat is chiefly used as a candle-making material.

Cocoa Nut Oil Group

The oils belonging to the cocoa nut oil group differ from all other vegetable fats by their high saponification and, consequently, high Reichert-Meissl values. Owing to their peculiar chemical composition (simulating to some extent that of butter fat) these oils are not readily saponified by weak caustic lyes. These fats require for saponification alkaline lyes of high strength, and are thereby so easily converted into soap that it is quite sufficient to stir the fats and caustic alkali well together and allow the mixture to stand. After some time saponification will take place with liberation of heat. (*Soap-making by the cold process.*) The soaps thus formed are very hard, and combine with a large amount of water without becoming soft. These soaps have further the remarkable property of requiring large quantities of salt to throw them out of their aqueous solution, hence they are used as "*marine soaps.*"

The following fats—arranged in the order of their iodine values —must be included in this group:—

(*a*) Muriti fat.
(*b*) Mocaya oil.

(*c*) Cohune oil.
(*d*) Maripa fat.
(*e*) Palm nut oil.
(*f*) Cocoa nut oil.
(*g*) Fat from *Cocos acrocomoides.*

(*a*) MURITI FAT[1]

French—*Huile de Muriti.* German—*Muritifett.*
Italian—*Burro di Muriti.*

Muriti fat is obtained from *Acrocomia vinifera*, a South American palm. The fat has a pleasant taste, and is similar to cocoa nut oil.

Physical and Chemical Constants of Muriti Fat

Specific Gravity at 25° C.	Melting Point. °C	Solidifying Point. °C.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.
0·9136	25	17	246·2	25·2	5

The specimen examined by *Fendler*[1] was prepared from a Nicaraguan fruit; it had an acid value of 1·69. The melting point of the fatty acids, obtained from three specimens, was 54·5° C; it is therefore likely that the fat contains myristic acid.

(*b*) MOCAYA OIL,[2] MOCAYA BUTTER

French—*Huile de mocaya.* German—*Mocayaoel.*
Italian—*Burro di Mocaya.*

Mocaya oil is obtained from the kernels of *Acrocomia sclerocarpa*, Mart. (*Cocos sclerocarpa, Cocos aculeata*, Jacq.), a palm-tree occurring in Paraguay and forming there vast forests. The kernels contain 60-70 per cent of fat.

This oil greatly resembles cocoa nut oil in its white colour, buttery consistence, and odour.

Physical and Chemical Constants of Mocaya Oil

Solidifying Point. °C.	Melting Point. °C.	Saponification Value. Mgrms. KOH.	Reichert-Meissl Value. c.c. $\frac{1}{10}$ norm. KOH.	Iodine Value. Per cent.
22	24-29	240·6	7·0	24·63

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[1] *Zeit. f. Unters. Nahrungs. und Genussm.*, 1903, 1025.
[2] De Negri and G. Fabris, *Giorn. farmac.* 1896, No. 12; *Chem. Rev.* 1897, 82.

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point. °C.	Melting Point. °C.	Neutralisation Value. Mgrms. KOH.
22-20	23-25	254
		Neutralisation Value of the Non-Volatile Acids. Mgrms. KOH.
		244·8

(*c*) COHUNE OIL

This oil is obtained from the kernels of the cohune palm, *Attalea cohune*, which grows abundantly in British Honduras.[1]

The kernels have the appearance of small cocoa nuts, their size is only that of large nutmegs. The kernels contain 40 per cent of a solid yellow fat, resembling in general appearance palm nut and cocoa nut oils.

Physical and Chemical Constants of Cohune Oil

Solidifying Point.	Melting Point.	Saponification Value.	Iodine Value.
°C. 16-15	°C. 18-20	219·4-220·5[2]	12·9-13·6

The mixed fatty acids melt between 27° and 30° C. The Reichert-Meissl value of the specimen of cohune oil described in the table had not been determined, but judging from the high saponification value that number will very nearly approach the Reichert-Meissl values of the other members of the cocoa nut oil group.

(*d*) MARIPA FAT[3]

French—*Huile de maripa*. German—*Maripafett*.
Italian—*Sego di Maripa*.

Maripa fat is obtained from the kernels of the *Palma* (*Attalea*) *maripa*, Aubl., a plant belonging to the palm family. It is indi-

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[1] *Bull. Imper. Inst.* 1903, xxv.

[2] Calculated by me from the saponification equivalent 253·9-255·3.

[3] Van der Driessen-Mareeuw, *Nederl. Tijdschr. Pharm.* 1899 (12), 245.

genous to the West Indies. Probably the commercial fat is also obtained from one or two other species of *Attalea*, viz., *A. excelsa*, Mart. (*Maximiliana maripa*, Drude) and *A. spectabilis*. The fat is obtained by expression or, in a cruder fashion, by boiling the fruit with water, when the fat rises to the top and is skimmed off. The expressed fat is colourless or faintly yellow; it has a mild taste and a faint, not unpleasant, odour.

Maripa fat is used as an edible fat in the West Indies and French Guiana; it is also used in pharmacy.

Physical and Chemical Constants of Maripa Fat

Specific Gravity. At 100° C. (water 15·5=1)	Solidifying Point. °C.	Melting Point. °C.	Saponification Value. Mgrms. KOH.	Iodine Value. Per Cent.	Reichert-Meissl Value. c.c. $\frac{1}{10}$ norm. KOH.	Hehner Value. Per Cent.	Observer.
	24-25	26·5-27	270·5	17·35 (?)	4·45	88·88	v.d. Driessen Mareeuw
0·8686		23	259·5	9·49			Bassière[1]

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity. At 100° C. (water 15·5=1)	Solidifying Point. °C.	Melting Point. °C.	Iodine Value.	Observer.
0·823	25	27·5-28·5	12·15 (?)	v. d. Driessen Marreeuw

(*e*) PALM KERNEL OIL, PALM NUT OIL

French—*Huile de palmiste*. German—*Palmkernoel, Kernoel.*
Italian—*Sego di noce di palma.*

For table of constants see p. 744.

Palm kernel oil is obtained from the kernels of the palm-tree fruit. The kernels are collected by the natives after the palm oil has been recovered from the fleshy part of the fruit; the shell is removed by the natives, and the kernels shipped to Europe. Recently a machine has been constructed for the breaking of the kernels on the spot, but in view of the exceedingly cheap labour (of women and children) it is to replace at West Africa, it is doubtful whether the machine will meet with extended application in the near future.

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[1] *Journ. Soc. Chem. Ind.* 1903, 1137.

The kernels are screened and then ground between rollers. The pulpy mass is either expressed in hydraulic presses or extracted with solvents. In the former process the meal must be pressed twice on account of the large proportion of fat the kernels contain.

The variations of the percentage of oil in the kernels will be gathered from the following two tables. The first table, due to *Fendler*,[1] refers to the varieties of palm fruits described above (page 706).

Variety.	Oil. Per cent.	Moisture. Per cent.
De	43·7	8·2
De de bakui	49·1	6·5
Se de	49·2	5·9
Afa de	45·5	6·5
Small-fruited Lisombe	49·2	...
Large-fruited Lisombe, ripe . . .	48·9	...
Large-fruited Lisombe, unripe . .	49·2	...

The numbers given in the following table, due to *Nördlinger*,[2] refer to commercial brands of palm kernels :—

Origin of Palm Kernels.	Proportion of Fat Per cent.	Origin of Palm Kernels.	Proportion of Fat Per cent.
Sierra Leone . . .	48·6	Togo District, French .	49·3
Island of Sherboro . .	46·7	Lagos	50·4
Liberia	49·4	Benin	49·8
Grand Bassa . . .	50·2	Niger	50·5
Half Jack	50·8	Brass	52·5
Apollonia	47·2	Calabar	50·9
Dixcove	48·2	Bonny	51·0
Cape Coast Castle . .	50·2	Opobo	52·3
Winnebah	46·1	Cameroons	49·0
Quitta	48·4	Congo	47·4
Togo District, German .	52·1	Loanda	50·9

The colour of palm kernel oil is white. In the fresh state the oil is neutral and has a pleasant smell and an agreeable nutty taste. Commercial samples contain, however, notable amounts of free fatty acids. The following table gives the proportions found in various samples of palm nut oil :—

Free Fatty Acids in Palm Kernel Oil

Kind of Oil.	No. of Samples.	Free Fatty Acids as Oleic Acid.	Observer.
		Per cent.	
	2	13·26-13·39	Salkowski
Expressed oil .	27	3·30-17·65	Nördlinger
,, ,, .	2	9·8 -11·16	Emmerling
Extracted oil .	10	4·17-11·42	Nördlinger
,, ,, .	5	6·38- 8·69	Emmerling
,, ,, .	4	3·29- 4·13	Fendler

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[1] *Berichte d. d. pharm. Gesellsch.* 1903, 115.

[2] *Journ. Soc. Chem. Ind.* 1895 585.

Emmerling[1] found the following increases in the amounts of free fatty acids in some specimens of oil kept in closed bottles for two years :—

Sample No.	Free Fatty Acid calculated as Oleic Acid.	
	Fresh Oil.	After Two Years.
	Per cent.	Per cent.
1	7·39	9·25
2	6·38	8·59
3	7·54	8·74
4	9·80	11·86

On exposure to the air for four months the amount of free fatty acids increased but little, viz.—from 8·59 and 8·74 to 9·10 and 10·00 per cent respectively; whilst the amount of volatile fatty acids measured by the Reichert-Meissl value increased after four months' exposure in the light from 5·96 and 5·41 to 6·69 and 6·38, and in the dark from 5·96 and 5·41 to 7·28 and 6·53 respectively.

Also the iodine values decreased on keeping in closed bottles, as shown in the following table :—

Sample No.	Iodine Value.	
	Fresh Oil.	Oil kept Two Years in Closed Bottle.
1	16·23	11·28
2	16·76	10·06
3	15·37	10·56
4	15·30	11·94

The chemical composition of palm kernel oil is not fully known. *Valenta*[2] examined the mixed fatty acids. By passing a current of steam through the acids a small quantity volatilised; the distillate consisted of *caproic* acid and most likely also of *caprylic* acid. After drying the acids that remained behind and distilling them fractionally, at a pressure of 100 to 160 mm., six fractions were obtained, the examination of which led to the results recorded in the table :—

Fraction No.	Boiling Point.	Melting Point.	Saponif. Value.	Iodine Value.	Yield.	Saturated Fatty Acids.	Oleic Acid.	Constituents of the Fraction
	°C.	°C.			Per cent.	Per cent.	Per cent.	
1	135-190	..	..	0	4	100	0	Caprylic, capric
2	190-200	31·5	310	2·6	10	97·2	2·8	Capric, oleic
3	200-205	37·5	275	3·4	58	96·3	3·7	Lauric, capric, oleic
4	205-225	32·5	264	7·8		91·5	8·5	" " "
5	225-245	31·5	251	16·7	15	81·7	18·5	Lauric, myristic, oleic
6	245-270	35·0	219	41·3	5	54·6	45·8	Myristic, palmitic, oleic
7	Residue	..	..	..	8	..	..	

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[1] *Landw. Versuchs. Stationen.* 1898, 51.

[2] *Zeit. f. angew. Chemie,* 1889, 335.

Physical and Chemical Constants of Palm Kernel Oil

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Hehner Value.		Refractive Index.	
°C.		Observer.	°C.	Observer.	°C	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	cc. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	At 60° C.	Observer
40 (water at 15·5=1)	0·9119	Allen	23·0[3]	Fendler	23-28	Valenta	247·6	Valenta	10·3-17·5	Valenta	5·0	Lewkowitsch	91·1	Lewkowitsch	1·4431	Thoerner.
99 (water at 15·5=1)	0·8731	,,	24·0[4]	,,	25-26	Thoerner	246-250	Thoerner	13·4-13·6	Morawski and Demski	5·41-5·96	Emmerling			Butyro-refractometer.	
			23·0[5]	,,	30·0[3]	Fendler	242·4-244·1	Lewkowitsch	13-14	Thoerner	5·85[3]	Fendler			At 40° C.	Observer.
			24·0[6]	,,	28·5[4]	,,	247·9	Emmerling	15·4-16·8[7]	Emmerling	6·34[4]	,,			36·5	Beckurts and Seiler
					29[5]	,,	254·8[1]		14·9[3]	Fendler	6·22[5]	,,				
					28[6]	,,	248·8[3]	Fendler	16·8[4]	,,	6·82[6]	,,				
							249·4[4]	,,	15·6[5]	,,						
							250·0[5]	,,	15·4[6]	,,						
							246·3[6]	,,								

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.		Refractive Index.	
°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.	At 60° C.	Observer.
Titer Test.		25-28·5	Valenta	258-265	Valenta	211	Valenta	12·07	Morawski and Demski	1·4310	Thoerner
20·0-20·5	Lewkowitsch	20·7	Thoerner	264	Thoerner	222·8	Lewkowitsch	12	Thoerner		
22·5-24·5	,,			251·7	Lewkowitsch						
23·5-24·5	,,										
24·6-25·5	,,										

[1] Extracted oil.

[2] Expressed oil.

[3] From De palm the oil contained 54·06 per cent free fatty acids (calculated to oleic).

[4] ,, De de bakui palm ,, ,, 55·07 ,, ,, ,, ,,

[5] ,, Se de palm ,, ,, 55·38 ,, ,, ,, ,,

[6] ,, Afa de palm ,, ,, 57·18 ,, ,, ,, ,,

[7] After keeping for two years in closed bottles these values had decreased cp. p. 743.

The chief constituent of palm kernel oil is therefore lauric acid. From the iodine value I calculate the proportion of olein as 12 to 20 per cent. The older statement of *Oudemans* that palm kernel oil contains 26·6 per cent of oleic acid, must be abandoned as erroneous. Palm kernel oil is very nearly related in its chemical composition to cocoa nut oil. Like the latter it is remarkable on account of its high saponification value, and the notable amount of glycerides of volatile fatty acids (cp. "Cocoa Nut Oil," p. 746). Like cocoa nut oil, it requires strong caustic soda lye for saponification, and yields a hard white soap, which is only thrown out in the "salting out" process by a large amount of salt.[1]

Palm kernel oil is largely used for soap-making. The freshest oil is employed in the manufacture of vegetable butter, like "Cocoa Nut Oil" (p. 752).

In this manufacture a hard fat ("*palm nut stearine*") is obtained: the liquid "*palm nut oleine*," being a by-product, is used in soap-making. A sample of palm nut oleine, examined by the writer, had the titer test 16·8° to 17° C.

Palm nut oil is not adulterated with other fats (cp. also p. 752). The edible variety of palm nut oil is, however, used for adulterating butter fat and cacao butter (see p. 726).

(*f*) COCOA NUT OIL

French—*Huile de coco*, *Beurre de coco*. German—*Kokosoel*, *Kokosnussoel*. Italian—*Burro di cocco.*

For tables of constants see pp. 747-749.

Cocoa nut oil is the fat obtained from the kernels of the cocoa nut, especially from those of the two species *Cocos nucifera* and *Cocos butyracea.*

In commerce three qualities of oil are distinguished: (1) *Cochin oil*, the finest and whitest quality, prepared in Cochin (Malabar).[2] The superiority of Cochin oil to Ceylon oil (2) seems to be due to some extent to the better climate, as the Malabar coast enjoys a larger number of dry months than Ceylon. Hence the kernels can be dried in the sun, whereby a whiter and better flavoured oil is obtained than the Ceylon oil quality. The superiority of Cochin oil is, however, chiefly due to better cultivation of the plant (manuring pruning, destruction of insects, etc.) and better and cleanlier methods of manufacture. The Cochin oil is also stated to contain a larger amount of "stearine" than the Ceylon oil. But this appears doubtful, and may be due to the larger yield of "stearine" obtainable on a large scale, owing to the smaller amount of free fatty

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[1] Cp. Lewkowitsch, *Journ. Soc. Dyers and Colourists*, 1894, March; *Journ. Soc. Chem. Ind.* 1894, 258.

[2] There are also the commercial brands: Cochin Australia, Cochin Mauritius.

acids than is found in Ceylon oils. (2) *Ceylon oil*, chiefly imported from Ceylon, where the fat is expressed or boiled out on a large scale. (3) *Copra oil*, the fat from the *copra*, *i.e.* the dried (sun-dried or kiln-dried) kernels, shipped in enormous quantities to Europe, where the oil is either expressed or extracted in a similar manner as described under "Palm Kernel Oil."

By expressing the kernels in the cold an oil of the solidifying point 13°-12° C., and the melting point 20° C. is obtained. This cold-pressed oil, however, is not a commercial product, being used where it is produced as a substitute for butter fat.

Cocoa nut oil is, in our climate, at the ordinary temperature a solid white fat. It has a bland taste, and, in its fresh state, a peculiar though not unpleasant odour. It turns, however, easily rancid, acquiring at the same time a disagreeable flavour and an acrid taste. Copra oil is richer in free fatty acids than Ceylon oil. The writer found in a large number of samples of copra oil free fatty acids to the extent of 25 per cent, whilst Ceylon oil as a rule only contained from 5 to 10 per cent of free acids calculated as oleic acid. The specimens examined by *Crossley* and *Le Sueur*,[1] contained from 5 to 17·7 per cent free fatty acids in terms of oleic acid.

Cocoa nut oil resembles palm nut oil in its chemical composition; like the latter it contains large proportions of trimyristin and trilaurin, smaller quantities of tripalmitin, tristearin, and triolein, as also the glycerides of the volatile caproic, caprylic, and capric acids. It is practically free from hydroxy acids[2] (*Lewkowitsch*).

The occurrence of tristearin is recorded here, as a specimen of commercial cocoa nut oil examined in my laboratory yielded 0·99 per cent of stearic acid. The occurrence of palmitic acid is doubtful (*Ulzer*[3]), but since the presence of stearic acid has been proved, his statement requires confirmation. The proportion of palmitic acid can only be small. *Tolman* and *Munson* obtained by the lead-salt-ether method 65·9 per cent of solid acids. The mean molecular weight of the volatile acids isolated by *Farnsteiner*[4] from a specimen of cocoa nut oil having the *Reichert-Meissl* value 6·6, is calculated as 156·8.

The amount of total volatile fatty acids found in my laboratory in the examination of a number of cocoa nut oils has been given above (chap. viii. p. 343).

The "titer test" of the fatty acids of cocoa nut oil varies according to the amount of washing given to the fatty acids in the course of their preparation. Thus a sample of cocoa nut oil, the fatty acids of which were washed as described in Chapter III. p. 62, had the titer test of 22°, whereas by washing with brine, in which the volatile fatty acids are less soluble than in water, a titer test of 21° was obtained. The respective mean molecular weights, calculated from the neutralisation values 261·4 and 267·7, were in the same order, 214·6 and 209·5.

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[1] *Journ. Soc. Chem. Ind.* 1898, 991. (The oleic acid numbers given in the original paper are wrong.)

[2] Unpublished experiments.

[3] *Chem. Rev.* 1899, 203.

[4] *Ibid.* 1898, 196.

Physical and Chemical Constants of Cocoa Nut Oil

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.	
° C.		Observer.	° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
15·5	0·9259	Tolman and Munson	20·5-16	Allen	20-28	Allen	257·3-268·4	Valenta	8·9	Hübl
			19·5-15·7	Valenta	23·5-24·1	Valenta	250·3	Moore	9-9·5	Thoerner
18	0·9250	Stilurell	16-14	De Negri and Fabris	26·2-26·4	Filsinger	washed oil		9-10	Lewkowitsch
40 (water at 15·5=1)	0·9115	Allen			24-27	De Negri and Fabris	246·2	,,	8·54[1]	Crossley and Le Sueur
			16-14	,,			253·4-262	De Negri and Fabris		
			20-16	,,	23-26	,,			8·41[2]	,,
99 (water at 15·5=1)	0·8736	,,	22-23	Thoerner	25-28	,,	255-260	Thoerner	8·25[3]	,,
					23-24	Thoerner	258·2[1]	Crossley and Le Sueur	8·74[4]	Wijs
					23·5-25	Crossley and Le Sueur			8·39[5]	,,
100 (water at 100=1)	0·9030[1]	Crossley and Le Sueur					255·6[2]	,,	8·84[6]	,,
							255·5[3]	,,	9·32[7]	,,
	0·9040[2]	,,								
	0·9042[3]	,,								

[1] Malabar oil.
[2] Bengal oil.
[3] Bombay oil.
[4] Cochin "neige."
[5] Cochin "prima."
[6] Ceylon oil.
[7] Ceylon prima.

Physical and Chemical Constants of Cocoa Nut Oil—continued

Reichert Value.		Hehner Value.		Refractive Index.			Viscosity.	
c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	At 60° C.		Observer.	Seconds at 140° F.	Observer.
3·7	Reichert	88·6-90·5	Lewkowitsch	1·441		Thoerner	63·9[1]	Crossley and Le Sueur
3·5-3·7	Allen Moore Muter	82·4[2]	Crossley and Le Sueur				64·7[2]	,,
		85·25[4]	Clapham				64·5[3]	,,
Reichert-Meissl Value.				Butyro-refractometer.				
				At ° C.		Observer.		
7·0	Lewkowitsch			15·5	49·1	Tolman and Munson		
7·5	Thoerner			40	33·5	Beckurts and Seiler		
6·71[1]	Crossley and Le Sueur			,,	35·5	Mansfeld		
6·79[2]	,,			,,	34·2	Crossley and Le Sueur		
6·65[3]	,,							
8·4	Ulzer							

[1] Malabar oil. [2] Bengal oil. [3] Bombay oil.

[4] Determined in my laboratory in a sample of commercial "cocoa nut oleine."

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.		Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.		Refractive Index.	
At 98°-99° C. (Water at 15·5=1.)	Observer.	° C	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.	At 60° C.	Observer.
0·8354	Allen	20·4	Hübl	24·6	Hübl	258	Thoerner	196-204	Alder Wright	8·39-8·79	Morawski and Demski	1·4295	Thoerner
		19·5-15·7	Valenta	24-25	Valenta			201	Williams	9·3	Williams		
		18-16	De Negri and Fabris	25-27	De Negri and Fabris			211[1]	Lewkowitsch	8·62-8·92	De Negri and Fabris		
		20	Thoerner	24-25	Thoerner					8·5-9	Thoerner		
		Titer Test.								Iodine Value of the Liquid Fatty Acids.			
		21·2-22·55	Lewkowitsch							36·3[2]	Clapham		
		21·9-24·7	,,							31·9	Tolman and Munson		
		23·0-23·6	,,										
		23·3-23·9	,,										
		23·9-25·0	,,										
		24·8-25·2 (Cochin)	,,										

[1] Ceylon oil.

[2] Determined in my laboratory in a sample of commercial cocoa nut oleine.

In the valuation of cocoa nut oil for soap-making, due regard must therefore be had to the manner in which the fatty acids are prepared for the titer test.

Cocoa nut oil is soluble in alcohol to a considerable extent, one volume of oil dissolving in two volumes of 90 per cent alcohol at 60° C.

Cocoa nut oil is chiefly used for soap-making and in the candle manufacture (night-lights); for the latter purpose the fat is subjected to hydraulic pressure, when a soft fat ("*cocoa nut oleine*") and a hard fat ("cocoa nut stearine") are obtained.

The following numbers have been ascertained in my laboratory by *Clapham* and by *Calderwood* for commercially prepared samples of "cocoa nut oleine" and "cocoa nut stearine":—

[Table

Fat

Cocoa Nut.	Specific Gravity.			Saponification Value.		Iodine Value.		Hehner Value.		Reichert-Meissl Value.	
	At °C.		Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.
"Oleine"	60	0·92931	Clapham	265·35	Calderwood	14·8	Calderwood	85·25	Clapham	7·95	Calderwood
"Stearine"				255·63	,,	4·0	,,			4·45	,,

Fatty Acids

Cocoa Nut.	Titer Test.		Neutralisation Value.		Mean Molecular Weight.	
	°C.	Observer.	Mgrms. KOH.	Observer.		Observer.
"Oleine"	20·6[1]	Calderwood	267	Clapham	210·0	Clapham
	20·1[2]	,,	266·9	,,	210·2	,,
	20·6	Clapham			204·6	Calderwood
"Stearine"	26·55[1]	Calderwood				
	26·42[2]	,,			211·4	,,

[1] Fatty acids washed with water.

[2] Fatty acids washed with brine.

Cocoa nut oil is also used extensively as an edible fat. For this purpose selected qualities of cocoa nut oil are employed, and the free fatty acids as also the objectionable odour of cocoa nut oil removed. During recent years large quantities of cocoa nut oil have appeared in the market under the names of "Vegetable Butter," "Mannheim Cocoa Nut Butter," "Lactine," "Vegetaline," "Nucoline," "Laureol," "Palmin," and a variety of other fancy names. These fats represent practically pure neutral cocoa nut oil; they are largely used in confectionery, and are also employed for the adulteration of butter fat (cp. chap. xv., Edible Fats).

The cocoa nut stearine obtained by expressing the more liquid portion of cocoa nut oil, is sold as cocoa butter substitute, chocolate fat, and is also largely used in adulterating genuine cacao butter (see chap. xv., Chocolate Fats).

Cocoa nut oil is not adulterated with other fats. Owing to the great similarity of cocoa nut oil with palm kernel oil, and the other oils of the cocoa nut oil group, the detection of palm kernel oil in cocoa nut oil, and *vice versa*, is a very difficult problem requiring extended research. Since cocoa nut oil and palm kernel oil are about the same price, and since the uses they are put to are practically identical, the examination of cocoa nut oil for admixtures with palm kernel oil, and *vice versa*, is but rarely required. It may assume importance in the examination of edible fats with a view to ascertaining their origin, as the properties of palm kernel oil and cocoa nut oil somewhat differ.

(*g*) The fat from *Cocos acrocomoides*, Dr., from Brazil was examined by *Niederstadt*.[1] Its iodine value was 4·8 and saponification value 292·8. The exceedingly high saponification value is probably due to the rancid state of the specimen, as its acid value was 131.

The *Reichert-Meissl* value of the sample was not determined; most likely it would have approximated that of the other fats belonging to the cocoa nut oil group.

TANGKALLAK FAT

German—*Tangkallakfett*.

This fat is obtained from the fruits of *Cylicodaphne sebifera* (*Cylicodaphne Litsæa*) Bl., a tree indigenous to Western Java, and at present common in Indo-China. The fruits yield 36·5 per cent (*Sack*), 40-45 per cent (*Lemarié*[2]) of a butter-like fat. According to *Sack*,[3] this fat contains 13·4 per cent of triolein and 80·6 per cent of trilaurin. From the proportion of triolein, I calculate the iodine value 11·54. The fat melts at 37° C. (*Sack*), 45° C. (*Lemarié*).

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[1] *Berichte d. deutsch. pharm. Gesellsch.* 1902, 144.

[2] *Bull. Imper. Inst.* 1903, 212. The spelling adopted there is tangkallah.

[3] *Pharm. Weekblad*, 1903, 4.

This fat is employed in the manufacture of candles and soap. *Lemarié* states that one tree is said to provide annually sufficient fat for the manufacture of 500 candles.

UCUHUBA FAT

French—*Graisse d'ucuhuba.* German—*Ucuhubafett.*
Italian—*Sego di Ucuhuba.*

For tables of constants see p. 754.

Ucuhuba fat is obtained from the nuts of *Myristica becuhyba* s. *officinalis.* The crude fat is yellowish-brown, and has an aromatic odour (due to a small quantity of an ethereal oil), recalling that of cacao.

Ucuhuba fat consists of myristin and olein (10·5 per cent), small quantities of an ethereal oil, of a resinous substance, and of a wax-like compound. The odour of the resinous substance resembles that of Peru balsam; it is soluble in ether, hot alcohol, petroleum ether, and chloroform.

The sample examined by *Valenta* contained 8·8 per cent of free fatty acids.

Ucuhuba fat is not identical with the fat from the "oil nuts," the seeds of *Myristica surinamensis.* The latter melts at 45° C., according to *Reimer* and *Will*,[1] and appears to have a similar chemical composition to that of ucuhuba fat, as it consists of almost pure myristin and a caoutchouc-like (resinous) substance.

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[1] *Berichte*, 1888, 2011.

[TABLE

Physical and Chemical Constants of Ucuhuba Fat

Solidifying Point.		Melting Point.		Saponific. Value.		Iodine Value.		Hehner Value.	
°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	Per cent.	Observer.
...	...	39	Valenta[1]	219-220	Valenta	9·5	Valenta	93·4	Valenta
32-32·5	Nördlinger	42·5-43	Nördlinger[2]						

Physical and Chemical Constants of the Mixed Fatty Acids

Melting Point.	
°C.	Observer.
46	Valenta
42·5-43	Nördlinger

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[1] *Jour. Soc. Chem. Ind.* 1889, 202.

[2] *Berichte*, 1888, 2617.

JAPAN WAX, JAPAN TALLOW

French—*Cire du Japon.* German—*Japanwachs, Sumachwachs, Japantalg.* Italian—*Cera giapponesa.*

For tables of constants see pp. 756, 757.

Japan wax is a hard, tallow-like mass which surrounds the kernels of the berries of several sumach trees, viz.—*Rhus succedanea, R. acuminata, R. vernicifera, R. sylvestris.*[1] The first three species grow chiefly in China, the last named one flourishes especially in the western provinces of Japan.

The manufacture of Japan wax is carried out in a somewhat crude fashion by storing the berries in straw until they have fully matured, then crushing them in a wooden, funnel-shaped trough by hand, and winnowing them to separate off the husk. The powdered mass so obtained is put into hempen sacks, and then subjected to pressure in wooden wedge presses.

With the growing demand for Japan wax the aim has been to increase the output; this is reached by mixing the press residue, or even the ground berries, with a certain proportion (usually 10 per cent) of perilla oil (see p. 444). This practice has been on the increase during the last ten years; therefore the discrepancies in the iodine values recorded in the table of constants are readily explained. Whereas the samples analysed by *Hübl* and by *Lewkowitsch* date back some decades, those having higher iodine values undoubtedly contained some traces of the perilla oil. Since perilla oil has so high an iodine value, it is evident that small quantities only are required to raise the iodine value of a specimen.

The berries yield from 15 to 25 per cent of a coarse, greenish, tallow-like mass. This is refined by remelting, pressing through cotton sacks, and allowing the fat to drop into cold water. The thin flakes of wax are then bleached by exposure to the sun in shallow baskets (in a similar manner as is done in the process of bleaching beeswax), the material is frequently turned over, and sprinkled with water. Finally the wax is melted and cast in slabs. In this form it is exported to Europe.

The imported Japan wax is a pale yellow, hard substance, of conchoidal, somewhat lustrous fracture. It has a wax-like consistence, and can be easily kneaded between the fingers. Its odour recalls that of tallow and beeswax.

On keeping, Japan wax turns deeper yellow, becoming coated with a white powder consisting of microscopical prismatic needles. Under the microscope Japan wax exhibits a crystalline structure.

The numbers for the specific gravity recorded in the table vary considerably; this is no doubt due to the samples having been derived from different sources.

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[1] This species occurs in Japan only, whereas the other species occur both in Japan and in China.

Physical and Chemical Constants of Japan Wax

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Hehner Value.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	Per cent.	Observer.
15	0·975	Dieterich	50·8	Rüdorff	50·4-51	Rüdorff	220	Hübl	4·2	Hübl	89·8	Lewkowitsch
15·5	0·984-0·993	Allen	53	Allen	56	Allen	214-221·3	Allen	4·9-6·6	Lewkowitsch		
			48·5	Eberhardt			221·6	Henriques	8·3-8·5	Geitel and van der Want	90·62-90·66	Geitel and van der Want
22	0·9692	Eberhardt			(cp. p. 757)		217·5-237·5	Geitel and van der Want	10·6-11·3	Bernheimer and Schiff		
,,	1·002	,,			52-53	Eberhardt	220·3-222·1	Bernheimer and Schiff	13·1-15·1	Ahrens and Hett		
60 (water 15·5=1)	0·9018	Allen			52·6-53·4	Bernheimer and Schiff						
98-99 (water 15·5=1)	0·8755	,,										
Bleached Japan Wax.												
22	0·9749	Eberhardt										

Refractive Index in Butyro-refractometer, observed at 84° C. and calculated to 40° C. :—47·6-49·7 (Berg, *Chem. Zeit.* 1903. 755).

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.		Solidifying Point.		Melting Point.		Mean Mol. Weight of the Insoluble Acids.	
At 98°-99° C. (water 15·5=1)	Observer.	°C.	Observer.	°C.	Observer.		Observer.
0·848	Allen	53·0-56·5	Allen	56-57 59-62	Allen Eberhardt	265·3 257·6 262-263	Allen Harris[1] Geitel and van der Want
		Titer Test.					
		58·8-59·4	Lewkowitsch				

Kleinstück[2] determined the specific gravity of several samples of Japan wax at different temperatures, and states that its density is equal to that of water at 16°-18° C.; below 16° C. it is heavier, and above 18° C. lighter than water. Japan wax which has been freshly melted has a higher specific gravity than the normal one, the density only becoming normal after keeping for some time. This phenomenon is due to the coëfficient of expansion of Japan wax being higher than that of water, as shown in the following table due to *Kleinstück*.

Specific Gravity of Japan Wax compared with that of Water at 4° C

Temperature. °C.	Japan Wax.		Water.
	Kept for some time.	Freshly melted.	
4	...	...	1·00000
6·5	...	1·00237	0·99995
7·2	1·00737	...	0·99991
17·0	...	0·99123	0·99884
17·5	0·99846	...	0·99875
23·0	...	0·98747	0·99762
26·5	0·98615	0·98683	0·99674

The melting points recorded in the table vary considerably. *Rouber's*[3] statement that Japan wax has two melting points, inasmuch

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[1] Determined in the writer's laboratory; the fatty acids had been previously freed from unsaponifiable matter. This specimen of Japan wax contained 1·1 per cent of unsaponifiable.

[2] *Journ. Soc. Chem. Ind.* 1890, 1072.

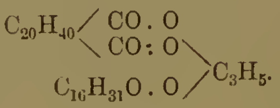
[3] *Journ. de Pharm.* [4] 16 (1872) 20.

as a specimen of the normal melting point melted immediately after solidification at 42° C., is due to the phenomenon described in Chapter I. *Eberhardt* also found that a specimen of the melting point 53° C. melted after rapid cooling at 48°-49° C.

Japan wax is insoluble in cold alcohol, but dissolves readily in boiling alcohol, separating on cooling almost completely as a granular, crystalline mass. Like all other fats it dissolves easily in ether, benzene, and petroleum ether. The following amounts of unsaponifiable matter were found by several observers:—

Unsaponifiable. Per cent.	Observer.
1·14	Allen and Thomson
1·1	Harris[1]
1·48-1·63	Geitel and v. der Want

Japan wax consists chiefly of palmitin and free palmitic acid. Besides these constituents, it also contains small quantities of Japanic acid (see p. 120) and soluble acids, most likely isobutyric acid (*Engelhardt*). *Geitel* and *v. der Want* found 4·66 to 5·96 per cent of soluble acids. Stearic and arachidic acids, previously stated to occur in Japan wax, could not be detected by *Geitel* and *v. der Want.* The Japanic acid very likely occurs as a mixed glyceride (*Geitel*) of Japanic and palmitic acids of the formula



$$\begin{array}{l} C_{20}H_{40}\diagup CO\,.\,O \\ \qquad\quad\;\; \diagdown CO\,.\,O\diagdown \\ \qquad\qquad\qquad\qquad\qquad C_3H_5. \\ \qquad C_{16}H_{31}O\,.\,O\diagup \end{array}$$

The amount of free fatty acids in commercial samples varies considerably, as shown in the following table:—

Free Fatty Acids. Per cent.	Observer.
9·13	Hübl
3·87	Nördlinger
8·96	Allen
9·03	,,
12·72	,,
9·40	Harris[2]
10·9-16·4	Geitel and v. der Want

Commercial Japan wax contains from 0·02-0·08 per cent of ash.

Japan wax is readily distinguished from true waxes by its saponification value and by its yielding glycerol on saponification; hence the name Japan tallow would appear to be preferable. Its detection in beeswax will be described pp. 897-898.

Adulteration of Japan wax with other fats is easily detected. The presence of tallow will be indicated by a low melting point and a high iodine absorption of the sample.

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[1] Determined in the writer's laboratory.

[2] The fatty acids had been previously freed from unsaponifiable matter.

Commercial Japan wax is frequently adulterated with from 15 to 30 per cent of water.[1] *La Wall*[2] found in a number of commercial samples starch to the extent of 20 to 25 per cent. On treating the adulterated wax with a solvent (p. 147) the fat only is dissolved. A more rapid method to detect starch is to moisten a freshly cut surface with iodine solution.

Japan wax is largely used for waxing floors, and as a constituent of polishes. Like beeswax and other animal waxes it forms an emulsion with water, and is therefore used for currying leather.[3]

MYRTLE WAX, LAUREL WAX, BAYBERRY TALLOW

French—*Cire de Myrica.* German—*Myrtenwachs, Myricawachs.*
Italian—*Cera mirica.*

For table of constants see p. 760.

Myrtle wax is obtained by boiling the berries of various species of *Myrica* (as *Myrica cerifera, M. carolinensis, M. caracassana, M. cordifolia, M. lacinata*) with water. The myrica shrubs are common along the Atlantic sea coast of America. Myrtle wax has a green colour, due to chlorophyll; on exposure to the air the uppermost layers are bleached to a whitish mass.

Myrtle wax is, chemically speaking, not a true wax.

Smith and *Wade*[4] ascertained that the myrtle wax fatty acids consist chiefly of palmitic acid. By recrystallising four times from petroleum ether, they obtained pure palmitin of the melting point 62·5° C., saponification value 209·4, and refractive index at 80° C. 1·4380. They further showed that by following *Hehner* and *Mitchell's* method no stearic acid was obtained. Judging from the low iodine value, small proportions of olein only can be present.

Smith and *Wade* observed notable changes in the melting point, they having obtained in the course of four months a rise in the melting point of myrtle wax of 4·45°. This phenomenon may be explained by the freshly melted palmitin having been converted on standing into its crystalline form (cp. p. 9).

The acid values of two specimens of myrtle wax examined by *Deering* were 3 and 4·4. The acid value of the specimen examined in my laboratory was 3·6.

Myrtle wax is useless as a candle material.

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[1] Wimmel, *Zeit. d. oest. Apothekervereins*, 1867, v. 350.

[2] *Journ. Soc. Chem. Ind.* 1897, 247.

[3] *Ibid.* 1898, 14.

[4] *Journ. Amer. Chem. Soc.* (1903) 629.

Physical and Chemical Constants of Myrtle Wax

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Refractive Index.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	At 80° C.	Observer.
15	0·995	Allen	39-43	Allen	40-44	Allen	205·7-211·7	Allen	1·95	Lewkowitsch	0·5	Smith and Wade	1·4363	Smith and Wade
22 (water at 15·5=1)	0·9806	Smith and Wade	45	Smith and Wade	48	Smith and Wade	217	Smith and Wade	3·9	Smith and Wade				
98-99 (water at 15·5=1)	0·875	Allen												
99 (water at 15·5=1)	0·878	Smith and Wade												

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Mean Molecular Weight.	
°C.	Observer.	°C.	Observer.		Observer.
46	Allen	47·5	Allen	243	Allen

Lesser Known Vegetable Fats

Fat.	Source.	Native Country.	Yield. Per cent.	Specific Gravity.	Saponification Value.	Iodine Value.	Hehner Value.	Reichert-Meissl Value.	Refractive Index.	Melting Point of Fatty Acids.	Acid Value.	Observer.
	Sterculia Chicha, St. Hil.	Brazil	...	...	194·15	78·9	...	...	...	...	...	Niederstadt
	Basiloxylon brasiliensis, K. Schumann . .	,,	...	...	197·25	76·4	...	...	...	...	...	,,
	Carpatroche brasiliensis, Endl.	,,	...	...	236·6	74·9	...	...	...	...	...	,,
	Ægiphila obducta, Vellos	,,	...	...	199·5	64·15	...	...	...	...	72·2	,,
	Chorisia Peckoltiana, Mart.	,,	...	...	216·2	61·4	...	...	...	...	13·1	,,
	Paullinea trigona, Vell. .	,,	...	...	...	57·65	...	...	...		16·55	,,
	Buchanania latifolia[1] .	North-West India	...	0·8942 at 100° (water 100=1)	193·6	57·3	95·8	0·33	1·4584	...	15-40	Crossley and Le Sueur
	Paneira do campa Bombax	Brazil	...	...	133	54·0	...	...	...	...	7·8	Niederstadt
	Pithecoctenium echinatum, K. Schumann .	,,	...	...	183·2	50·7	...	...	...	...	51·5	,,
	Carica papaya, L. . .	,,	...	...	186·58	50·7	...	...	...	...	83·7	,,
Kanya butter Sierra Leone butter Lamy butter .	Pentadesma butyracea, Don.	West Africa	47-50									
Wild olive fat[2] . .	Simaruba . . .	San Salvado	...	...	...	...	...	...	...	48-49[3]		
Undung tallow Labreu tallow (Bői-lói) .	Tetranthera[4] laurifolia, Jacq.	Asia[5]										
Advocate pear[6] . .	Persea gratissima . .	Brazil										

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[1] Melting point 32° C.

[2] Melting point 30° C.

[3] The solid portion of the mixed fatty acids melted at 64°-55° C. (*Journ. Soc. Chem. Ind.* 1902, 1164). They were fractionated by means of the barium salts into three portions, melting at 58°-59° C., 44° C., and 38° C. respectively.

[4] *T. citrata*, Nees., *T. glabraria*, Nees., and *T. Roxburghii*, Bl. yield similar products (*Bull. Imper. Inst.* 1903, 212).

[5] The plant has also been introduced into America.

[6] This is a corruption of the Brazilian word "aguacata." The fat from the pulp of the fruit is edible and known as vegetable butter. Its cultivation has been extended to most tropical countries; it is common in Indo-China.

Lesser Known Vegetable Fats—See Table.

2. ANIMAL FATS

The fats described under this head vary in their hardness, like the vegetable fats, in inverse proportion to the amount of unsaturated fatty acids they contain, or, in other words, to the amount of iodine they absorb. Butter fat, in a similar fashion as the fats of the cocoa nut oil group, occupies an exceptional position owing to its high proportion of volatile acids. In a system based on similarity of chemical composition butter fat would be classed with the cocoa nut oils, but it is more convenient to retain a subdivision into vegetable and animal fats, inasmuch as these two classes can be readily differentiated by the phytosteryl acetate test.

The unsaturated fatty acids of the animal fats were until recently considered to consist of oleic acid only, and this was thought to constitute an important natural difference between vegetable and animal fats. It has, however, been shown that some animal fats contain less saturated fatty acids than oleic acid. Indeed, the presence of linolic acid has been proved in the case of lard (*Fahrion*) and hare fat (*Kurbatoff*), by identifying amongst the oxidation products of the liquid fatty acids sativic acid, and, in the case of lard, by the isolation of linolic tetrabromide (*Farnsteiner*). Furthermore, *Farnsteiner* has shown that even small quantities of linolenic acid occur in lard and tallow (for a probable explanation, see below). From icebear fat 9·3 per cent of fatty acids were isolated, the iodine value of which even reached as high a figure as 244·4.

We are, therefore, in a position to discriminate drying, semi-drying, and non-drying fats, similarly as in the case of vegetable oils and fats, and also to establish among the animal oils and fats all gradations from fish and liver oils down to the hardest fats, containing very small percentages of glycerides of unsaturated fatty acids. Whilst the marine animal oils simulate the drying oils, we have a certain class of animal fats, represented by icebear fat, blackcock fat, hare fat, wild duck fat, which may be likened to semi-drying oils. Reasoning by analogy, we must ascribe these drying properties to the occurrence of fatty acids, which are less saturated than oleic acid.

The presence of highly unsaturated fatty acids in icebear fat suggests the inference that the nature of the food has great influence on the chemical composition of the body-fat. On this assumption *Voit's* opinion that each animal is characterised by a specific kind of fat is no longer tenable. Although this question would appear to belong to the domain of physiology, its discussion is germane to our subject, inasmuch as it is a matter of the greatest importance to the analyst in case he has obtained abnormal numbers in the examination of a lard or butter fat.

It is well known that if large quantities of one particular fat are given with the food, such fat is liable to pass into the body-fat of the animal. Thus it has been shown that the fat from dogs who were given in their food considerable quantities of linseed oil had acquired the peculiar odour of linseed oil, and exhibited distinct drying properties; again, after feeding them with rape oil the presence of erucic acid in the fat was proved. It has further been ascertained that hogs fed on dried fish yielded lard of a disagreeable fishy taste, and moreover such lard was less hard than lard from normally fed hogs. During the last decade or two the practice of feeding the hogs (in America) on maize has produced much "softer" lards than were previously obtained, a fact which must undoubtedly be ascribed to the influence of maize oil.

It has also been observed that tallow from cattle fed on oil cakes is softer, *i.e.* richer in olein, than tallow from cattle fed on grass (South American tallow, New Zealand tallow). Not only does the kind of food influence the character of the body-fat, but, as a general rule, the fat given in the food seems also to pass into the milk fat.[1] Thus *Baumert* and *Falke*[2] have shown that on feeding cows with oil-cake obtained from sesamé seed, almonds, and cocoanuts, there were obtained butter fats which showed so remarkable a decrease in their proportions of volatile fatty acids (*Reichert-Meissl* values) that without further investigation the butter fats would have been declared adulterated, inasmuch as the analytical characteristics were those of a mixture of genuine butter fat with very considerable amounts of foreign fats (cp. also "Human Fat," p. 774).

The above mentioned occurrence of linolenic acid in lard and tallow can therefore be explained by the influence of the food on the body fat (cp. also "Lard," p. 789, "Butter Fat," p. 883). In order to further illustrate the influence of the food, I collate some isolated observations on the fats from certain wild animals, and contrast them with the fats from the same species in a domesticated state.

Fat from		Iodine Value.
Rabbit,	wild	101·1
,,	tame	64·4
Goose,	wild	99·6
,,	wild, held in captivity 2 years	67·0
,,	domestic	67·6
Duck,	wild	84·6
,,	domestic	58·5
Hog,	wild	76·6
,,	domestic	63 (max.)
Cat,	wild	57·8
,,	domestic	54·5

In the case of wild goose and wild duck, the feeding on fish satisfactorily explains the high iodine values.

As a corollary to the foregoing observations, it may be added

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[1] Cp. Zuntz and Usson., *Chem. Centralblatt.* 1900, 382; Einecke, *Mitth. d. Landw. Inst.* 1903, 559.

[2] *Zeit. Unters. Nahrgs. u. Genussm.* 1898, 665.

that the fat from a chicken fed on milk gave a larger amount of volatile fatty acids than ordinary chicken fat (*Zaitschek*).[1] Experiments made by *Wieser and Zaitschek*[2] on geese fed with maize showed, however, that the body fat was not altered.[3] As a further general rule it may be stated that the amount of liquid (unsaturated) fatty acids decreases as the position of the fat approaches the warmest parts of the body.[4]

In view of the change animal fats undergo in consequence of the change of food, it became of great importance to investigate whether phytosterol passes, together with a vegetable fat supplied in the food, into the body fat, and may therefore occur in such body fat together with cholesterol. This possibility was not at all unlikely, since the colouring matter contained in cotton seed and cotton seed oil passes into the body fat of hogs, and into the milk fat of cattle fed on cotton seed cake. *C. Virchow*[5] has, however, shown that on feeding animals (dogs, hogs, etc.) with cotton seed oil and peas, phytosterol could not be detected in the body fat.

I subdivide the animal fats into: (1) drying, (2) semi-drying, and (3) non-drying fats.

(1) Drying Animal Fats

Fats.	Specific Gravity.	Saponification Value.	Iodine Value.	
	At 15° C.	Mgrms. KOH.	Per cent.	Observer.
Icebear	0·9256	187·9	147·0	H. Bull
Rattlesnake	0·9217	210·9	105·58	Kebler and Pancoast

(2) Semi-drying Animal Fats

Kind of Fat.		Specific Gravity. at 15° C.		Solidifying Point.		Melting Point.		Saponification Value. Mgrms. KOH.		Reichert Value.	Iodine Value. Per cent.	
	German.	Fat.	Fatty Acids.	Fat °C.	Fatty Acids. °C.	Fat °C.	Fatty Acids. °C.	Fat.	Fatty Acids.	c.c. $\frac{1}{10}$ normal KOH.	Fat.	Fatty Acids.
Blackcock	Auerhahn	0·9296	0·9374	..	25-28	..	30-33	201·6	199·3	2·10	121·1	120
Wild duck	Wildente	..	..	15-20	30-31	..	36-40	198·5	..	1·30	84·6	..

Observers—Amthor and Zink.

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[1] *Pflüger's Arch.* 98, 1903, 614.

[2] *Ibid.* 1902, 128.

[3] Cp. also Paraschtschuk, *Chem. Centralbl.* 1903, i. 731; Arnold, *Ibid.* 1903, i. 531.

[4] Henriques and Hansen, *Biederm. Centr.* 1901, 182; Lemmermann and Linkh, *Landw. Jahrbücher*, 1903, 635.

[5] *Zeit. Unters. Nahrgs. u. Genussm.* 1889, 559.

HORSE FAT

French—*Graisse de cheval.* German—*Pferdefett.*
Italian—*Grasso di cavallo.*

For tables of constants see p. 766.

Fresh horse fat is of a yellowish colour, and has a buttery consistence. On standing it separates into a solid and a liquid portion. In its fresh state it is neutral. As the rendering of horse fat is not so carefully carried out as that of other animal fats, remnants of tissue are frequently contained therein. Hence it readily becomes rancid.

In a sample of kidney fat *Hehner* and *Mitchell* could not detect stearic acid. *Farnsteiner* isolated from a specimen of horse fat linolic tetrabromide in a quantity corresponding to 9·9 per cent linolic acid in the fat.

The occurrence of linolic acid satisfactorily explains the weak drying properties horse fat shows on exposure to the air.

In consequence of the increasing consumption of horse meat, horse fat has become a commercial article. It is used by the poorer classes on the Continent as an edible fat in place of lard, and is no doubt used as an adulterant of more expensive fats.

The following constants for horse fat from various parts of the body[1] have been published by various observers :—

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[1] As to the foot oil, cp. p. 685.

[Table

Horse Fat from	Consistence.	Colour.	Specific Gravity.		Solidifying Point. °C.	Melting Point. °C.	Solidifying Point of Fatty Acids. °C.	Melting Point of Fatty Acids. °C.	Saponific. Value.	Iodine Value of		Reichert Value.	Hehner Value.	Acid Value.	Observer.
			At °C.							Fat.	Fatty Acids.				
Kidneys	Salve-like, soft	Golden yellow	15	0·9320	22	39[1]	30-30·5	36-37	198·7	81·09	83·88	0·33	95·47	1·73	Amthor and Zink
,,	..	..	..	..	..	..	..	.	..	85·4	..	..	..	..	Hehner and Mitchell
,,	..	..	17·5	0·9212	48-47	53-54	..	..	187·6	82·6	84·0	..	..	..	Frühling
,,	..	..	50	0·8987	..	..	..	..	..	..	..	..	..	..	,,
Neck .	Like fresh hard butter	Deep orange-yellow	15	0·9330	30	34-45[1]	32-33	41-42	199·5	74·84	74·41	0·22	95·42	2·44	Amthor and Zink
Leaf .	Butterlike	Golden Yellow	15	0·9319	20	36-37[1]	31-32·5	39-40·5	197·8	81·6	83·37	0·38	94·78	1·84	,,
Back .	..	..	17·5 50	0·9159 0·8963	45-43	52-53	..	..	182·8	79·9	81·4	..	..	..	Frühling
Heart .	..	..	17·5 50	0·9167 0·8948	34-32	40-41	..	..	184·7	77·4	78·3	..	..	..	,,

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[1] Capillary tube method.

Physical and Chemical Constants of Horse Fat

Specific Gravity.			Melting Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Hehner Value.		Refractive Index. Butyro-refractometer.		Maumené Test.	
At °C.		Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	At 40° C.	Observer.	° C.	Observer.
15	0·9189	Filsinger	20	Lenz	197·1	Filsinger	86·1	Kalmann	1·64-2·14	Kalmann	96-97·8	Kalmann	53·7	Mansfeld	46-54·2	Gill and Rowe
,,	0·916-0·922	Gill and Rowe	41·8-43·2[1]	Kalmann	195·1-196·8	Kalmann	84	Filsinger							Specific Temperature Reaction.	
98-99	0·861	Allen					71·4-72·4	Lewkowitsch								
100	0·798-0·799	Gill and Rowe					75·1-86·3	Gill and Rowe							95·8-114	Gill and Rowe

[1] Capillary tube method.

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.	
°C.	Observer.	°C.	Observer	Mgrms. KOH.	Observer.	Per cent.	Observer.
37·3-37·7	Kalmann	37·5-39·5	Kalmann	202·6-202·7	Kalmann	83·9-87·1	Kalmann
33·6-33·7 (Titer Test)	Lewkowitsch						

HARE FAT

French—*Graisse de lièvre.* German—*Hasenfett.*
Italian—*Grasso di lepre.*

For tables of constants see p. 768.

Hare fat (obtained from several specimens) is, according to *Amthor* and *Zink*,[1] pale yellow to orange-yellow in colour. It is of soft consistence, and separates on standing into a thick yellow oil and a white crystalline deposit. Even in the fresh state it has a disagreeable rancid smell, which becomes more unpleasant on standing.

Exposed in a thin layer—spread on a glass plate—hare fat dries in about 8 days to a tolerably viscid varnish, becoming solid after 4 more days. The iodine number after 38 days' exposure was 19·4.

Hare fat contains linolic acid (p. 761).

The acid value of the specimen examined by *Amthor* and *Zink* was, in the fresh state, 2·73, and 8 after 6 months.

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[1] *Zeit. f. analyt. Chemie*, 1897, 8.

[TABLE

Physical and Chemical Constants of Hare Fat

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Reichert Value.		Hehner Value.		Refractive Index.	
															Butyro-refractometer.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per Cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per Cent.	Observer.	At 40° C	Observer.
15	0·9349	Amthor and Zink	17-23[1]	A. and Z.	35-40[1]	A. and Z.	200·9	A. and Z.	102·2	A. and Z.	1·59	A. and Z.	95·2	A. and Z.	49	Drumel
100	0·861	Drumel.	28-30	Drumel	44-46	Drumel					Reichert-Meissl Value.		95·5	Drumel		
											2·64	Drumel				

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.		Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.		Refractive Index.	
										Butyro-refractometer.	
At 15° C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per Cent.	Observer.	At 40° C.	Observer.
0·9361	Amthor and Zink.	36-40[1]	A. and Z.	44-47[1]	A. and Z.	209·0	A. and Z.	93·3	A. and Z.	36	Drumel
		39-41	Drumel	48-50	Drumel						

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[1] Capillary tube method.

RABBIT FAT

French—*Graisse de lapin.* German—*Kaninchenfett.*
Italian—*Grasso di coniglio.*

For tables of constants see p. 770.

This fat is of a dirty yellow colour; on standing, it separates into a liquid and a solid portion.

The fat from the wild rabbit differs very notably from that of the tame rabbit in the iodine value. On exposure to the atmosphere the fat from the wild animal dries after 7 days to a nearly solid varnish, becoming completely solid after 6 more days. After 50 days' exposure the iodine number was only 26. The fat from the tame animal does not exhibit drying properties.

The acid values of the wild rabbit fat and tame rabbit fat were 7·2 and 6·2 respectively.

As a rule, the fat of domesticated animals is richer in olein than that of wild animals, but in this case as well as in that of the wild goose the reverse obtains.

Physical and Chemical Constants of Rabbit Fat

Source.	Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Reichert Value.		Hehner Value.		Refractive Index. Butyro-refractometer.	
	At °C.		Observer.	°C.	Observer.	°C.	Observer.	M'ms. KOH.	Observer.	Per Cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per Cent.	Observer.	At 40° C.	Observer.
Wild Rabbit	15	0·9393	Amthor and Zink[1]	17-22[2]	A. and Z.	35-38[2]	A. and Z.	199·3	A. and Z.	99·8	A. and Z.	0·7	A. and Z.	..	..		
Tame Rabbit	15	0·9342	,,	22-24[2]	,,	40-42[2]	,,	202 6	,,	67·6	,,	2·8	,,	..	..		
												Reichert-Meissl Value.					
	100	0·861	Drumel[3]	28-30	Drumel	44-46	Drumel	..	..	..	..	2·64	Drumel	95·5	Drumel	49	Drumel

Physical and Chemical Constants of the Mixed Fatty Acids

Source.	Specific Gravity.		Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.		Refractive Index. Butyro-refractometer.	
	At °C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per Cent.	Observer.	At 40° C.	Observer.
Wild Rabbit .	0·9246	Amthor and Zink	35-36[2]	A. and Z.	39-41[2]	A. and Z.	209·5	A. and Z.	101·1	A. and Z.		
Tame Rabbit .	0·9264	,,	37-39[2]	,,	40-42[2]	,,	218·1	,,	64·4	,,		
			39-41	Drumel	48-50	Drumel					36	Drumel

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[1] *Zeit. f. analyt. Chemie*, 1897, 9.

[2] Capillary tube method.

[3] *Bulletin de l'Assoc. Belge*, 1896 (9), 323.

(3) NON-DRYING ANIMAL FATS

HORSE MARROW FAT[1]

French—*Moëlle de cheval.* German—*Pferdemarkfett.*
Italian—*Grasso di midollo di cavallo.*

Physical and Chemical Constants of Horse Marrow Fat

Specific Gravity.	Solidifying Point.	Melting Point.	Saponification Value.	Iodine Value.	Reichert Value.
At 15° C.	°C.	°C.	Mgrms. KOH.	Per Cent.	c.c. $\frac{1}{10}$ norm. KOH.
0·9204-0·9221	24-20[2]	35-39[2]	199·7-200	77·6-80·6	1·0

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.	Solidifying Point.	Melting Point.	Neutralisation Value.	Iodine Value.
At 15° C.	°C.	°C.	Mgrms. KOH.	Per Cent.
0·9182-0·9289	36-34[2]	42-44[2]	210·8-217·6	71·8-72·2

Horse marrow fat is pale yellow. A specimen of freshly rendered fat had the acid value 1·0, and a sample three months old 0·8.

GOOSE FAT

French—*Graisse d'oie.* German—*Gänsefett.* Italian—*Grasso d'oca.*

For tables of constants see pp. 772, 773.

Goose fat is a semi-pellucid, pale yellow fat of granular structure. It consists of olein, palmitin, stearin, and small quantities of glycerides of volatile acids.

The proportion of soluble fatty acids varies, according to *Young*, from 0·7 to 3·5 per cent, calculated as oleic acid.

There are added in the tables some constants of the fat from the wild goose; it would follow from the iodine value that the fat of the wild goose is richer in olein than that of the domesticated goose.

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[1] Zink, *Forschungsberichte über Lebensmittel*, etc., 1896, 441.

[2] Capillary tube method.

Physical and Chemical Constants of Goose Fat

	Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.	
	At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.
Domesticated goose	37·8 (water at 37·8=1)	0·909	Young	...	...	...	...	192·6	Valenta
,,	...	...	...	...	...	33-34	Bensemann	184-198	Young
,,	15	0·9229-0·9300	Rözsényi	18·1-18·4	Rözsényi	27·5-31·7	Rözsényi	191·2-193	Rözsényi
,,	15	0·9274	Amthor and Zink	18-20	Amthor and Zink	32-34	Amthor and Zink	193·1	Amthor and Zink
Wild goose . .	...	...	...	18-20	,,	...	...	...	...
Wild goose, 2 years in captivity .	15	0·9158	,,	...	...	...	...	196	,,

Physical and Chemical Constants of Goose Fat—continued

	Iodine Value.		Reichert-Meissl Value.		Hehner Value.		Refractive Index. Butyro-refractometer.	
	Per Cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per Cent.	Observer.	At 40° C.	Observer.
Domesticated goose	71·5	Erban and Spitzer	...	...	95·88	Bensemann	...	...
,,	...	. .	...	...	92·4-95·7	Young	...	...
,,	58·7-66·4	Rözsényi	0·2-0·3	Rözsényi	94·5-95·3	Rözsényi	50-50·5	Rözsényi
,,	67·6	Amthor and Zink						
Wild goose . .	99·6	,,						
Wild goose, 2 years in captivity .	67·0	..						

Physical and Chemical Constants of the Mixed Fatty Acids

	Specific Gravity.		Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.	
	At 15° C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per Cent.	Observer.
Domesticated goose .	...	...	...	...	37-38 and 40-41	Bensemann	...	...	...	...
,, .	...	...	...	...	36·6-49·2	Rözsényi	...	...	...	...
,, .	0·9257	Amthor and Zink	31-32	Amthor and Zink	38-40	Amthor and Zink	202·4	Amthor and Zink	65·3	Amthor and Zink
Wild goose . .	...	...	33-34	,,	34-40	,,	...	...	...	...
Wild goose, 2 years in captivity . .	0·9251	,,	32	,,	36-38	,,	196·4	,,	65·1	,,

HUMAN FAT

French—*Graisse d'homme.* German—*Menschenfett.*
Italian—*Grasso d'uomo.*

For tables of constants see p. 775.

Human fat was first examined by *Chevreul* and afterwards by *Heintz.*

The consistence of human fat approaches that of butter. On crystallisation from ether *Mitchell*[1] obtained a slight deposit of crystals, melting at 51·5° C.; under the microscope these crystals somewhat resembled those frequently obtained from flare lards. *Partheil* and *Ferié*[2] obtained pure tripalmitin by removing the liquid portion by expression and crystallising the solid portion from absolute alcohol. In the liquid portion dioleo-stearin (p. 16) was identified. Human fat may therefore be considered as consisting chiefly of tripalmitin and dioleo-stearin; neither myristic nor lauric acids were fonnd by the lithium salt method. In the light of these numbers the statement made by *Jaeckle*[3] that the mixed fatty acids consist of 4·9-6·3 per cent of stearic acid, 16·9-21·1 per cent of palmitic acid, and 65·6-86·4 per cent of oleic acid must be accepted with reserve. The amonnt of unsaponifiable matter in human fat was found by *Jaeckle* 0·33 per cent; the proportion of lecithin calculated from the phosphorus contents was 0·084 per cent.

The iodine value of the fat of new-born babies was found by *Knöpfelmacher* as 43·3.[4] The proportion of liquid acids increases, however, rapidly, until at an age of one year the fat has the iodine value of 65 (67·25 *Langer*), which is the iodine value of the fat from adults. The fat of well-fed children is richer in oleic acid than that of underfed ones. The influence of food on the iodine value of the fat is further clearly illustrated by the statements made by *Rosenfeld*[5] that the fat of Polynesians, living chiefly on cocoa nuts, resembled somewhat cocoa-nut oil, whereas the fat obtained from an Eskimo had the iodine value 79, thus showing the influence of the blubber oil in the consumed food.

With the decomposition of the human body setting in, the tissue disappears first, and the more resistant fat is converted into the so-called *adipocere*, a hard wax-like mass consisting chiefly of fatty acids. *Schmelck*[6] has examined three specimens of adipocere, with the following result:—

Melting point, 62·5° C.; insoluble fatty acids (*Hehner* value), 83-84 per cent; ash, 1·64-1·79 per cent (containing 83-84 per cent CaO); unsaponifiable, 16·7 per cent; acid value, 197; saponification value of the fatty acids, 202·8-203·4; iodine value, 14-14·2; iodine value of the fatty acids, 14·4.

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[1] *Analyst*, 1896, 172.
[2] *Archiv d. Pharmacie*, 1893, 545.
[3] *Chem. Zeit.* 1897, 163.
[4] *Chem. Centr.* 1898, i. 788.
[5] *Chem. Zeit.* 1902, 1110.
[6] *Chem. Zeit.* 1902, 11.

Physical and Chemical Constants of Human Fat

	Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Hehner Value.		Thermal Test.		Refractive Index. Butyro-refractometer.	
	At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per Cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per Cent.	Observer.	Heat of Bromination. °C.	Observer.	At 40° C.	Observer.
Adult	15	0·9179	Jaeckle[1]					193·3-19·9	Jaeckle			0·25-0·55	Jaeckle						
	25 (water 25° = 1)	0·9033	Mitchell[2]	15	Mitchell	17·5	Mitchell	195 196·25-198·1	Mitchell Partheil and Ferié	61·5 57·21-66·31	Mitchell Partheil and Ferié	0·5 1·12-2·12	Mitchell Partheil and Ferié	93·92-96	Partheil and Ferié	11·3	Mitchell	49·6-53	Mitchell
New born babies								204·3	Jaeckle	47·3-58·1	Jaeckle	1·75-3·4	Jaeckle						

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.	Melting Point.	Iodine Value.	Observer.
°C.	°C.	Per cent.	
30·5	35·5	64	Mitchell
		Iodine Value of the Liquid Fatty Acids.	
		92·1	,,

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[1] *Chem. Zeit.* 1897, 163.

[2] *Analyst*, 1896, 172.

LARD

French—*Saindoux.* German—*Schweinefett.* Italian—*Strutto.*

For tables of constants see pp. 777-779.

Lard is the fat rendered from the leaf of the pig, *i.e.* the fat from the kidneys and the bowels. This is the fat sold as home-rendered lard. There are, however, enormous quantities of lard imported by the large American packing-houses (in Chicago and elsewhere) that does not represent lard as defined here. In the retail trade we find the following brands of American lard:—(1) "Bladder lard," this being the best quality, it should be or approaches lard proper; (2) "Keg lard," containing, besides leaf lard, the fat from other parts of the animal. The following grades of lard are known in the American packing-trade:—

(*a*) *Neutral Lard No.* 1.—This consists of the fat from the leaf of the slaughtered animal, rendered in a perfectly fresh state at a temperature between 40° to 50° C. This lard is practically neutral, and is used almost exclusively in the manufacture of margarine ("oleo-margarine").

(*b*) *Neutral Lard No.* 2.—This is the back fat rendered in the same careful manner as Neutral Lard No. 1. It is chiefly used for the purposes of confectioners and biscuit bakers.

(*c*) *Leaf Lard* (German—*Speckschmalz*).—On subjecting the residue not rendered for neutral lard to steam heat under pressure, the leaf lard of commerce is obtained. Formerly this was the only kind of lard recognised by the Chicago Board of Trade, and was then prepared from the whole leaf. "Bladder lard" is most likely "leaf lard."

(*d*) *Choice Lard, Choice Kettle-rendered Lard.*—This kind of lard is obtained from the remaining portions of the leaf (after the fat for "oleomargarine" (see (*a*)) has been rendered), together with the fat cut from the backs (see (*b*)). It takes its name from the process, being rendered in steam-jacketed open kettles. According to the regulations of the Chicago Board of Trade, choice lard is defined as lard made from leaf and trimmings only, either steam- or kettle-rendered; the manner of rendering must be branded on each tierce. Its flavour is much superior to that of prime steam lard.

(*e*) *Prime Steam Lard* (German—*Dampfschmalz*).—This is defined thus: Standard prime steam lard is the product of the trimmings and other fat parts of hogs, rendered in tanks by the direct application of steam, etc.—This lard is passed solely on inspection, and as the inspector has no authority enabling him to supervise rendering establishments, in order to secure a proper control, we may take it that prime steam lard consists of the fat from any part of the hog, either from the whole animal or from portions of it (head, foot).

A lower quality still is made from "*guts*" only.

Lard possesses a granular texture and a salve-like consistence. It has a pure white colour. The lard rendered from the leaf and

Physical and Chemical Constants of Lard

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.	
° C.		Observer.	° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.
15	0·931-0·932	Hager	27·1-29·9	Goske	42-48	Koenigs	195·3-196·6	Valenta
40 (water at 15·5=1)	0·8985	Allen			45-46	Bensemann	195·2-196·2	Lewkowitsch
50 (water at 50=1)	0·89159-0·90038	Fairley and Cooke			36-45·5	Dieterich		
90	0·894-0·897	Dieterich						
98-99 (water at 15·1=1)	0·8608	Allen						
100 (water at 15=1)	0·861	Koenigs						
100	0·8610-0·8614	Gladding						
100 (water at 15=1)	0·8589-0·8641 [1] (American)	Dennstedt and Voigtländer						
			Fat from	*Wild Boar*				
15	0·9424	Amthor and Zink	22-23	Amthor and Zink	40-44	Amthor and Zink	195·1	Amthor and Zink
			27·9-30·8 [3]	Richardson [2]	32-37·5 [3]	Richardson		
			24·7-27·3 [4]	,,	32 [4]	,,		

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[1] In one case 0·8700 was found.

[2] *Journ. Amer. Chem. Soc.* 1904, 372.

[3] From leaf.

[4] From back.

Physical and Chemical Constants of Lard—continued

Iodine Value.		Reichert Value.		Hehner Value.		Maumené Test.	Refractive Index.		
Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.			At 60° C.	Observer.
49·9-63·8	Dieterich			95·8	Bensemann	(See Table, p. 791.)		1·4539	Thoerner
62·4 (American)	Schweitzer and Lungwitz			93-98	Wiley			Oleo-refractometer.	
60·4-70·4 (American)	Raumer							"Degrees."	Observer.
59-68·4 (American)	Dennstedt and Voigtländer							−12·5	Jean
55 (European)	,,						Butyro-refractometer.		
53-76·9	Lewkowitsch						At ° C.	"Degrees."	Observer.
(Cp. also pp. 787-789.)							40	50-51·2	Benedikt and Wolfbauer
							,,	48·6-51·2	Mansfeld
							,,	44·8-53	Dennstedt and Voigtländer
							25	56·8-58·5	Spaeth
	Fat from	*Wild Boar*							
76·6	Amthor and Zink	0·68	Amthor and Zink						
78·8-82[1]	Richardson								
81·5-84·7[2]	,,								

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[1] From leaf.

[2] From back.

Physical and Chemical Constants of the Mixed Fatty Acids

	Specific Gravity.			Solidifying Point.		Melting Point.		Mean Molecular Weight.		Iodine Value.		Thermal Test. Heat of Bromination.		Refractive Index.	
	° C.		Observer.	° C.	Observer.	° C.	Observer.		Observer.	Per cent.	Observer.	° C.	Observer.	At 60° C.	Observer.
	99° (water 15·5=1)	0·837-0·840	Allen	34 39 39 41·45-42 (Titer test) 36·0 [2]	Mayer Allen Terreil Lewkowitsch ,,	35 44 43 43-44 and 46-47	Mayer Allen Terreil Bensemann	278	Allen	64·2	Williams	10·4-11	Hehner and Mitchell	1·4395	Thoerner.
										Iodine Value of the Liquid Fatty Acids.				Oleo-refractometer.	
														"Degrees."	Observer.
										89·4-90·7 (European) 93-96 (European) 103-105 (American) 96·9-103·2 (American) 93·5-103·7 (European) 95·2-104·9 (American) 92-115·5 [2] (European-American) 97·0 [3] 99·8 [4]	Dieterich Wallenstein and Finck v. Raumer Bömer ,, Lewkowitsch Tortelli and Ruggeri			– 30	Jean
														Butyro-refractometer. See p. 793.	
														Refractive Index of the Liquid Fatty Acids.	
														Butyro-refractometer.	
										Fatty Acids.				At 40° C.	Observer.
														43·1-44·7 44-45	Bömer Mansfeld
Wild boar	15	0·9333	Amthor and Zink	32·5-33·5	Amthor and Zink	39-40	Amthor and Zink	275·5 [1]	Amthor and Zink	81·2	Amthor and Zink				

[1] Calculated from saponific. value 203·6. [2] Iodine value of lard 76·9. [3] Genovese lard of iodine value 57·5. [4] Iodine value of lard 63·2.

even from the back has an agreeable taste. The lower qualities have an insipid taste at first; this disappears, however, on standing.

Lard consists of the glycerides of lauric, myristic, palmitic, stearic, and oleic acids, and small quantities of linolic acid (and perhaps also of linolenic acid). The proportion of stearic acid in a number of commercial lards determined by *Hehner* and *Mitchell's* method,[1] varied from 6 to 24·91 per cent. The statement made first by *Fahrion*, viz. that lard contains linolic acid, is confirmed by the fact that the liquid fatty acids of lards, especially of American lards, have iodine values varying from 93-106, and reach even, as I have ascertained recently, 115·5.

Farnsteiner found in a specimen of European lard (iodine value 51·4) the following percentages of solid and liquid acids :—

	Solid Fatty Acids.	Liquid Fatty Acids.
	Per cent.	Per cent.
Lard I. (iod. val. 51·4)	41·3	53·7 (iod. val. 93)
,, II. . . .	42·2	53·1

The 53·1 parts liquid fatty acids of Specimen II. were resolved by the barium-salt-benzene method into 39·2 parts of oleic acid and 13·9 parts of less saturated acids. The presence of linolic acid was proved by the isolation of linolic tetrabromide. Since a brominated acid of the melting point 165° C. was isolated, the inference is justified that this product represents a mixture of linolic tetrabromide and linolenic hexabromide.

Twitchell[2] calculated the composition of a lard (iodine value of the mixed fatty acids = 62·57) as follows :—

Linolic acid	10·06 per cent.
Oleic acid	49·39 ,,
Solid acids (difference) . . .	40·55 ,,

The iodine values of the two fractions of liquid acids he prepared were 109·35 and 118·02.

The composition of an American lard, absorbing 65·78 per cent iodine, is given by *Partheil* and *Ferié*[3] as follows :—

Stearic acid	8·16- 8·64 per cent.
Palmitic acid	4·36- 4·59 ,,
Myristic acid	14·03-14·68 ,,
Lauric acid	13·08-10·27 ,,
Unsaturated acids . . .	53·73-54·37 ,,
	93·36-92·55 ,,

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[1] *Analyst*, 1896, 326 ; 1902, 248.

[2] *Journ. Soc. Chem. Ind.* 1895, 515 ; cp. 2nd edition of this work, p. 202.

[3] *Arch. d. Pharm.* 1903, 566.

Kreis and *Hafner* have proved the occurrence in lard of a mixed glyceride ("Daturodistearin," p. 16).

The analytical differences between lards from different parts of the hog are summarised in the following tables. Since important differences exist between North American and European lards, owing to the mode of fattening, I consider it useful to differentiate as far as possible between European and American lards.

European Lards

Fat from	Spec. Grav. at 100° C. (Water 15=1.)	Melting Point of Fat.	Melting Point of Fatty Acids.	Iodine Value of		Free Fatty Acids.		Observer.	Remarks.
				Fat.	Fatty Acids.	c.c. norm. KOH per 100 grms.	Calculated to Oleic Acid.		
		°C.	°C.				Per cent.		
Back .	0·8607	33·8	40	60·58	61·90	0·54	0·152	Spaeth	Mean results from examination of fats from 8 animals.
Kidney .	0·8590	43·2	43·2	52·60	54·20	0·58	0·163	,,	
Leaf .	0·8588	44·5	42·9	53·10	54·40	1·28	0·360	,,	

North American Lards

Fat from	Specific Gravity at 100° C. (Water at 15° C=1.)	Iodine Value.	Maumené Test at 40° C.	Melting Point (Bensemann's Method).		Refractive Index.	Observer.
				Drop formed at °C.	Melted to a clear drop. °C.	Butyro-refractometer at 40° C.	
						"Degrees."	
Head	0·8637	66·2	33	24	44·8	52·6	Dennstedt and Voigtländer
	0·8629	66·6	32	24	44·8	52·5	
	0·8631	65·0	34	24	45·0	52·0	
Back	0·8611	61·5	37	28·5	48·5	52·4	
	0·8621	65·0	35	28·5	48·5	51·8	
	0·8616	65·1	38	31·5	46·0	51·9	
Leaf	0·8637	62·2	...	26	45	51·4	
	0·8615	59·0	...	29	44	50·2	
	0·8700	63·0	30	28·5	44·5	52·0	
Foot (hoof)	0·8589	68·8	...	24	40	44·8	
Ham	0·8641	68·4	38	26	45	51·9	
	0·8615	66·6	...	26	44	51·9	
	0·8628	68·3	...	26	44·5	53·0	
Ham (German)	0·8597	55·0	30	32	46	49·2	Dennstedt and Voigtländer

As a corollary to these tables, I add the following table, due to *Hehner* and *Mitchell*,[1] setting out the percentages of stearic acid in

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[1] *Analyst*, 1896, 326.

lards taken from various parts of a hog (Somersetshire, six months old):—

Fat from	Melting Point. °C.	Iodine Absorption.	Stearic Acid.	
			Per cent.	Melting Point. °C.
Head	34·8	67·7	8·67-9·47	67·8-66·2
Ham	34·6	61·6	8·74-9·02	67·5-67·3
Breast	36·8	64·2	11·84-10·9	67·2-66·8
Flare	40·0	52·8	15·7-14·4	66·5-67·2
Back	35·6	67·9	8·59-9·2	67-66·5

Pure lard contains small quantities of unsaponifiable matter. *Allen* and *Thomson* found 0·23 per cent., *Lewkowitsch* 0·35 per cent. The bulk of the unsaponifiable matter consists of cholesterol.

Freshly rendered lard is practically neutral; determinations of the free fatty acids made by several chemists gave the following numbers:—

Free Fatty Acids as Oleic Acid.	No. of Samples.	Observer.
Per cent.		
0·280-0·420	?	Dieterich
0·350-1·000	12	Wiley
0·098-0·564	24	Spaeth

The increase of acidity on exposure to air in loosely corked flasks is numerically shown in the following table, together with the fluctuations in the iodine number (*Spaeth*):—

No.	Free Fatty Acids; c.c. norm. KOH per 100 grms.			Iodine Value.			
	Freshly rendered.	After one year.	After three years.	Freshly rendered.	After one year.	After three years.	
						Fat.	Liquid Fatty Acids.
1	0·6	6·4	32·0	63·25	53·80	39·26	74·51
2	0·45	2·75	23·0	61·15	55·45	39·37	74·60
3	0·75	7·80	31·6	62·90	51·85	39·56	72·48
4	0·80	11·60	50·0[1]	62·95	48·80	29·41	
5	1·25	6·70	36·0	57·25	49·40	26·51	64·30
6	0·35	6·00	30·0	55·88	47·80	31·19	
7	0·45	8·40	23·0	60·10	51·04	41·08	69·20
8	0·55	21·20	41·3	55·80	37·50	22·97	
9	1·45	1·80	10·0	52·30	52·20	40·91	
10	0·55	9·60	30·0	57·08	46·70	33·69	
11	1·60	15·40	46·0	51·75	36·71	21·56	
12	0·65	9·60	33·0	63·61	49·00	38·04	
13	0·60	4·20	18·0	52·35	46·85	36·48	
14	0·50	7·60	32·0	60·95	52·72	36·03	

[1] Corresponding to 14 per cent of oleic acid.

The free fatty acids were separated into soluble and insoluble acids by washing the lards with hot water. Their relative proportions were measured by the amounts of normal alkali required to saturate the free acids. The following table gives the details :—

No.	Free Fatty Acids after three years' exposure.	Soluble Fatty Acids.	Insoluble Fatty Acids.[1]
	c.c. normal Alkali per 100 grms.	c.c. normal Alkali. per 100 grms.	c.c. normal Alkali per 100 grms.
1	32·0	4·5	27·5
2	23·0	4·7	18·3
3	31·6	4·2	27·4
4	50·0	8·1	41·9
5	36·0	6·6	29·4
6	30·0	4·0	26·0
7	23·0	3·4	29·6
8	41·3	7·4	33·9
9	10·0	1·9	8·1
10	30·0	3·9	26·1
11	46·0	7·1	38·9
12	33·0	4·1	28·9
13	18·0	2·1	15·9
14	32·0	4·4	27·6

Lard (like butter and olive oil) is adulterated on the largest scale. Beef fat, beef stearine, cotton seed oil, cotton seed stearine, and other vegetable oils are the most frequently used adulterants. In the United States of America admixture with foreign fats and oils has become an openly acknowledged practice, nay, it has even been claimed that the addition of cotton seed oil constitutes an improvement in the manufacture. Thus the American brand "refined lard" was found to be a mixture of lard with cotton seed oil and a sufficient quantity of beef stearine to obtain the consistence possessed by pure lard. Owing to the interference of the law in this and other countries, the name "refined lard" has been abandoned, and has been replaced by such terms as "compound lard" or "lard compound." Some of these artificial preparations did not even contain any lard at all, being judiciously prepared mixtures of beef stearine and cotton seed oil or cotton seed stearine.

Water, which was often used as an adulterant is, at any rate in American lards, not common. Adulteration of this kind, as perhaps also the addition of arachis oil (*Wiley*), may be practised on a small scale, but is of little importance commercially.

I shall consider here chiefly the sophistication with vegetable oils (notably cotton seed oil and cotton seed stearine) and beef stearine. With regard to the latter it should be mentioned that the admixture of 5 per cent of beef stearine, as a "stiffener," is openly advocated by the trade as a necessary operation.

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[1] Evidently found by difference.

Artificial lard, that is, a product prepared from vegetable oils (cotton seed oil, arachis oil, etc.) and beef stearine, solidifies to a coarsely crystalline mass, exhibiting a more or less polished surface, whereas genuine lard, whether crude or refined, shows a finely crystalline texture and a dull, wrinkled surface (*Langfurth*[1]). Very little importance should be attributed in an examination of a sample to indications of this kind, for at present the lard in the large slaughter-houses, when running out of the rendering kettle, is cooled artificially and stirred mechanically so as to acquire a granular texture. A differentiation of genuine lard from adulterated lard on the strength of the consistence may have been approximately possible at the time when American hogs were fed on wheat and the lard was hard, but since fattening with maize and also cotton seed or cotton seed cake has been resorted to, the consistence has gradually become that of soft butter.

The following physical and chemical methods are of use in the detection of adulterants in lard:—

Specific Gravity.—The specific gravity should only be considered as a useful corroboration of other tests, since some of the usual adulterants have nearly the same specific gravity as pure lard. However, cotton seed oil raises the specific gravity, as also does arachis oil. Therefore a sample having a higher specific gravity than 0·861 at 100° C. must be looked upon with suspicion.

The following table contains some specific gravities, reference to which will be found useful:—

Specific Gravity of Lard, Lard Adulterants, and Compound Lards

Kind of Fat.	Specific Gravity at °C.			Observer.
	37·8° (100° F.) (Water 37·8=1.)	99° (Water 15·5=1.)	100° (Water 40=1.)	
Pure lard	0·905-0·907	0·860-0·861	0·85997-0·86191	Allen, Pattinson, Crampton
Lard stearine	..	..	0·8575-0·85792	Crampton
Cotton seed oil	..	0·868-0·8725	0·8672	Pattinson, Allen
,,	..	..	0·86681-0·86774	Leone and Longi
Cotton seed stearine	0·911-0·912	..	0·86463	Allen, Crampton
Beef stearine	..	0·8570	0·85444-0·85888	Pattinson, Crampton
Arachis oil	..	0·8673	..	Allen
Cocoa nut oil	0·910-0·916	0·8736	..	,,
Armour's compound lard	..	..	0·86121-0·86222	Crampton
Fairbanks' ,, ,,	..	..	0·86289	,,

Fairley and *Cooke*[2] have determined the specific gravities at 50° C. of the following mixtures of lard and cotton seed oil:—

[TABLE

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[1] Cp. also Soltsien, *Pharm. Ztg.* 1894, 350.
[2] *Journ. Soc. Chem. Ind.* 1890, 1162.

Mixtures of	I. Lard, 0·90038; Cotton Seed Oil, 0·90879.	II. Lard, 0·89159; Cotton Seed Oil, 0·89992.
Lard with 10 per cent of cotton seed oil .	0·90116	0·89246
,, 20 ,, ,, ,, .	0·90209	0·89328
,, 30 ,, ,, ,, .	0·90302	0·89421
,, 50 ,, ,, ,, .	0·90494	0·89617
,, 75 ,, ,, ,, .	0·90736	0·89850

Melting Point.—Although the melting point of a sample is not of itself of great importance (many adulterated lards having the same melting points as pure lard), still its determination should not be omitted. In the case of unadulterated hog's fat it is possible to ascertain from what part of the body the fat has been rendered; this will be seen by a glance at the following table:—

Melting Points of Lards from different parts of Hogs—
North American and European

Source.	Fat from	Melting Point. °C.	Observer.[1]
American .	Foot (hoof)	35·1	Wiley
	Head	35·5	,,
	Leg	42·5	
	Ham	44·5	
European .	Back	33·8	Spaeth
	Kidney	43·2	,,
	Leaf	44	,,

Goske,[2] taking the solidifying point of lard similarly as is done in the "Titer test," gives the following numbers:—

Fat.		Solidifying Point. °C.
Home-rendered lard	European .	27·10-28·62
,, ,,	,, .	26·64-29·34
,, ,,	,, .	29·10-29·95
Pure steam lard	North American .	24·10-26·00
,, ,,	,, .	25·05-25·5
,, ,,	,, .	26·40-27·06
,, ,,	,, .	24·9
,, ,,	,, .	23·67-26·18
Adulterated lard .	. . .	30·50
,, ,, .	. . .	29·73-29·80
,, ,, .	. . .	29·90-30·15
,, ,, .	. . .	31·95-33·00
,, ,, .	. . .	35·90-36·58
,, ,, .	. . .	35·50-35·75

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[1] Cp. also Dennstedt and Voigtländer's table, p. 781.

[2] *Journ. Soc. Chem. Ind.* 1893, 470.

The adulterant in the last instances was tallow, the presence of which was masked by the addition of lard oil.

Iodine Value.—In the present state of lard production it is not possible to lay down limits within which the iodine values of commercial samples may vary. As the lowest limit of the iodine value of European lard, 46 was given in the last edition of this work. During the last few years, however, genuine lards rendered in my laboratory, from the leaf only, gave as high values as 53 - 60·44. The iodine value of the liquid fatty acids of the leaf-lard absorbing 60·44 per cent was 94·11 only. Nor can the upper limit of 63, given in the last edition of this work, be maintained, as during the last few years North American lards of grade (*d*) (p. 776), having iodine values exceeding even 70, have been imported. A specimen of North American lard examined recently in my laboratory absorbed 76·9 per cent iodine (iodine value of liquid fatty acids 115·5). Still, a specimen of lard, the iodine value of which falls outside of the range 50 to 66, should be looked upon with suspicion or at best as inferior lard (see table, p. 787). Of course, the converse does not follow, *i.e.* that a sample of an iodine absorption within the limits named, must be pure, as combinations of fats of low (tallow, cocoa nut oil) and high absorptions (cotton seed, arachis, maize oils) enable the adulterator to prepare a variety of mixtures which will satisfy the limits laid down above. *Therefore a normal iodine absorption cannot be considered of itself as a final proof of purity.* Thus in the case of artificial lards made from steam lard, tallow stearine, and lard oil, to the exclusion of vegetable oils, the iodine value will, as a rule, lie approximately within the above-named limits. The following table, due to *Goske*, gives the iodine values of several artificial lards calculated from those of its components, based on the following iodine numbers:—beef stearine, 20; steam lard, 65; mutton tallow, 40; lard oil, 85.

Fat.	Beef Stearine.	Steam Lard.	Mutton Tallow.	Lard Oil.	Calculated Iodine Value.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1	10	90	...	...	60·5
2	15	85	...	...	58·25
3	...	70	30	...	57·50
4	25	45	...	30	59·75
5	35	25	40	...	57·27

The influence of exposure of lard on the iodine value may be gathered from the table, p. 782.

Provided adulterations with foreign fats be excluded, it is possible to ascertain with some measure of accuracy by means of the iodine value, from what part of the animal the lard has been derived. This is shown in the following table:—

[Table

Source.	Fat from	Iodine Value.	Observer.
North American .	Head	85·03	Wiley
		66·2-70·4	v. Raumer
		65·0-66·6	Dennstedt and Voigtländer
		66·0-69·7	Mans
		63	Dupont
	Foot (hoof)	77·28	Wiley
		69·5-69·6	v. Raumer
		68·8	Dennstedt and Voigtländer
		69·4	Mans
		65	Dupont
	Back	63·6-66·7	v. Raumer
		64·7-66·3	Mans
		61·5-65·1	Dennstedt and Voigtländer
		61	Dupont
	Leaf	58	,,
		53·1	Spaeth
		52·55	Wiley
		60·4-66·7	v. Raumer
		59-63	Dennstedt and Voigtländer
		63·3-65·0	Mans
	Ham	67·7-69·0	v. Raumer
		66·6-68·4	Dennstedt and Voigtländer
		68·4-70·4	Mans
	Guts	60	Dupont
South American .	Head	59·7	Tortelli and Ruggeri
	Back	56·0	,, ,,
	Paunch	58·2	,, ,,
	Leaf	54·2	,, ,,
European—German .	Back	53·0-58·5	v. Raumer
		61·7	,,
	Leaf	50·4	,,
	Ham	55·0	Dennstedt and Voigtländer
Italian .	Head	59·2-68	Tortelli and Ruggeri
	Back	60·5-64·4	,, ,,
	Paunch	61-69·0	,, ,,
	Leaf	53·1-57·4	,, ,,

Steam lard, consisting as it does of the mixed fats from all or at least different parts of the animal, may therefore in some cases have a normal value, say up to 63, in other cases it may absorb more iodine, even as much as 76·9 (*Lewkowitsch*).

It will thus be obvious that the iodine value of the fat affords but limited information. Nor can the determination of the iodine value of the liquid fatty acids, which up to recently *did* furnish *reliable* indications of admixture of vegetable oils and fats with lard, be considered as leading to a definite decision regarding the presence of adulterants. Whereas up to a few years ago the rule held good that in the case of European lards the iodine value of the liquid fatty acids varied between 90 and 96, and in the case of American lards between 95·2 and 106, these limits no longer hold good; for, whilst *Bömer* found in a Westphalian lard, rendered by himself, the iodine value of the liquid fatty acids at 103·5, *Lewkowitsch* found in a North American lard as high a number as 115·5.

In order to emphasise this point, I have compiled the following tables:—

Fat or Oil.	Iodine Value of		Observer.
	Fat.	Liquid Fatty Acids.	
Lard, "Western Steam Lard"	65·4	104·5	Wallenstein and Finck[1]
,, American (18 samples)	58·4-62·9	95·2-104·9	Bömer[2]
	...	98-115·5	Lewkowitsch
,, Berlin	52·7	96·6	Wallenstein and Finck
,, Vienna	60·9	95·2	,,
,, Hungarian	60·4	96·2	,,
,, Roumanian	59·5	96·0	,,
,, Bavarian (5 samples)	52·2-61·2	92·8-96·6	v. Raumer[3]
,, Westphalian	52	93·5-103·7	Bömer
,, South American	...	92·8-100·6	Tortelli and Ruggeri
,, Italian	...	92-105·3	,,
Beef tallow, Australian	38·3	92·2	Wallenstein and Finck
,, Berlin	45·2	92·4	,,
,, Hungarian	38·6	92·7	,,
Cotton seed oil, American, white	108·0	147·5	,,
,, ,, ,, yellow	107·8	147·3	,,
,, ,, Egyptian, bleached	106·5	146·8	,,
,, ,, ,, yellow	108·0	148·2	,,
,, ,, Peruvian	106·8	147·8	Bömer
,, ,,	104·6-105·7	141·9-144·5	Wallenstein and Finck
Niger seed oil	133·5	147·5	,,
Maize oil	122·0	140·7	,,
Arachis oil	98·9	128·5	,,
Rape oil	101·1	120·7	,,
Olive oil	79·3-81·7	96·4-96·7	Bömer
Cocoa nut oil	8·0	54·0	Wallenstein and Finck

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[1] *Journ. Soc. Chem. Ind.* 1894, 79.

[2] *Zeits. f. Unters. der Nahrungs. u. Genussm.* 1898, 539.

[3] *Zeits. f. angew. Chemie*, 1897, 210.

[Table

Source.	Fat from	Iodine Value of		Observer.
		Fat.	Liquid Fatty Acids.	
North American	Head I.	70·0-70·4	102·4	v. Raumer[1]
	,, II.	66·2-66·4	97·8-97·6	,,
	,, III.	68·2-68·4	101·2	,,
	Back I.	64·6-64·9	101·6-101·0	,,
	,, II.	63·6-63·6	102·8-102·3	,,
	,, III.	66·5-66·7	100·6-101·1	,,
	Leaf I.	66·4-66·7	103·0-102·6	,,
	,, II.	62·7-62·9	97·8-97·8	,,
	,, III.	60·7-60·4	96·9	,,
	Foot	69·5-69·6	98·6-98·3	,,
	Ham I.	67·9-67·9	101·6-101·0	,,
	,, II.	67·9-67·7	99·9-100·2	,,
	,, III.	68·7-69·0	103·0-103·2	,,
South American	Head	59·7	100·6	Tortelli and Ruggeri[2]
	Back	56·0	96·4	,, ,,
	Paunch	58·2	99·1	,, ,,
	Leaf	54·2	92·8	,, ,,
Italian . .	I. Head	68·0	98·2	Tortelli and Ruggeri
	Back	64·4	104·2	,, ,,
	Paunch	66·6	105·3	,, ,,
	Leaf	57·2	93·3	,, ,,
	II. Head	65·9	98·0	,, ,,
	Back	63·9	98·5	,, ,,
	Paunch	67·4	99·3	,, ,,
	III. Head	59·2	95·5	,, ,,
	Back	60·5	100·6	,, ,,
	Paunch	61·0	97·9	,, ,,
	Leaf	53·1	92·0	,, ,,
	IV. Head	65·6	103·3	,, ,,
	Back	61·9	102·3	,, ,,
	Paunch	69·0	104·9	,, ,,
	Leaf	57·4	94·0	,, ,,

The wide variations which the iodine values of the liquid fatty acids exhibit at present, no longer afford the same certainty in judging a sample of lard as they did a few years ago; we must even expect that the iodine values of genuine lards will slowly move in the direction of the upper limits. Whilst, then, the iodine value of the liquid fatty acids does not afford a definite means of detecting adulteration, still the determination of this value should not be omitted, since it furnishes additional evidence in the examination of those samples which must be regarded with suspicion. If the iodine value of the liquid fatty acids of a sample be found much above 110, adulteration with vegetable oils—such as cotton seed oil, maize oil—must be suspected. On the other hand, if the iodine value of the liquid fatty acids lies much below 90, admixture with cocoa nut oil or palm kernel oil must be assumed.

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[1] *Zeits. f. angew. Chemie*, 1897, 210.

[2] *L'Orosi*, 1900, April.

It must, however, be repeated that if the iodine value of a sample under examination is found within the permissible limits, the lard cannot yet be pronounced unadulterated. For any admixed vegetable oil may have been compensated by cocoa nut oil or to some smaller extent by beef tallow.

This test must, therefore, be supplemented in doubtful cases by special tests for cocoa nut oil and tallow (see below).

Thermal Tests.—As a preliminary test, and in cases where a large number of samples must be examined in a short time, the rise of temperature on mixing with concentrated sulphuric acid or with bromine will be found to furnish useful results in a short time; this holds especially good of the second reagent.

Maumené Test.—The rise of temperature found on mixing the sample with sulphuric acid has been recommended for the detection and even approximate estimation of cotton seed oil in lard by *Hehner*, *Ambühl*, *Wiley*, and *Engler* and *Rupp*, whereas *Williams* failed to obtain decisive results.

The numbers obtained by different experimenters vary so considerably, that the safest plan will be to make comparative tests with pure specimens of lard and cotton seed oil before examining the sample. It need hardly be mentioned that the sample must be thoroughly dry before testing. The following table contains a few numbers obtained by various observers:—

Fat.	Rise of Temp. °C.	Method Employed.	Observer.
Lard	24-27·5	50 grms. of fat; 10 c.c. conc. H_2SO_4	Hehner
Cotton seed oil	70	,, ,, ,,	,,
Lard	13-15	,, ,, ,, initial temp. 40° C.	Ambühl
Cotton seed oil	50-52	,, ,, ,, ,, ,, ,,	,,
"American" lard	30-35	,, ,, ,, ,, ,, ,,	,,
Lard	41·5	,, ,, ,, ,, ,, 35° C.	Wiley
Cotton seed oil	85·4	,, ,, ,, ,, ,, ,,	,,
Steam lard	38·8-42·1	,, ,, ,, ,, ,, ,,	,,
"Oleostearine"	20·8	,, ,, ,, ,, ,, ,,	,,
Lard stearine	37·7	,, ,, ,, ,, ,, ,,	,,
Artificial lards	42·1-58·9	,, ,, ,, ,, ,, ,,	,,
,, ,,	51·3-68·8	,, ,, ,, ,, ,, ,,	,,
Lard	31-32	,, ,, ,, ,, ,, not stated	Engler and Rupp
Cotton seed oil	81	,, ,, ,, ,, ,, ,,	,,
Lard with 10 per cent of cotton seed oil	34	,, ,, ,, ,, ,, ,,	,,
,, ,, 20 ,, ,, ,,	40-42	,, ,, ,, ,, ,, ,,	,,
,, ,, 50 ,, ,, ,,	58	,, ,, ,, ,, ,, ,,	,,
Lard	35	,, ,, ,,[1] ,, ,, 35° C.	Schweitzer and Lungwitz
Lard oil	45·3	,, ,, ,, ,, ,, ,,	
"Oleostearine"	31·9	,, ,, ,, ,, ,, 45° C.	,,
Cotton seed oil	61·5	,, ,, ,, ,, ,, 35° C.	,,
Armour's compound lard	58·0	,, ,, ,, ,, ,, ,,	,,
Tallow	31·6	,, ,, ,, ,, ,, 45° C.	,,

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[1] Acid of 100 per cent H_2SO_4, prepared by mixing fuming acid with conc. commercial acid.

In order to obtain more decisive results the liquid portion obtained by expression may be examined as well (*Langfurth*).

Heat of Bromination.—The following numbers were obtained by *Hehner* and *Mitchell*;[1] the iodine values calculated from the temperatures observed are collated with those actually found with *Hübl's* solution:—

Fat.	I. Heat of Bromination. Rise of Temperature	II. Iodine Value. Experiment.	III. Iodine Value calculated from I.
	° C.	Per Cent.	Per Cent.
Lard No. 1	10·6	57·15	58·3
,, 2	10·4	57·13	57·2
,, 3	11·2	63·11	61·6
,, 4	11·2	61·49	61·6
,, 5	11·8	54·69	64·9
,, 6	11·8	63·96	64·9
,, 7	10·2	57·15.	56·1
,, 8	10·4	57·80	57·2
,, 9	9·0	50·38	49·5
,, 10	11·0	58·84	60·5
Lard + 10 per cent cotton seed oil	11·6	64·13	63·8

Refractometric Examination.—The refractometric examination will be usefully employed as a preliminary or, in doubtful cases, as a corroborative test. The numbers recorded in the following tables may therefore be found useful. It should be noted that the difference between European and American lards is not quite so distinctly shown in the refractometric constants as in the iodine absorption numbers.

Refractive Indices determined by means of the Butyro-refractometer.

Kind of Fat.	European.		American.	
	Scale Divisions at 40° C.	Observer.	Scale Divisions at 40° C.	Observer.
Lard from head	...	...	52-52·6	Dennstedt and Voigtländer
,, ,, back	50·2-50·4	Mansfeld	51·8-52·4	,,
,, ,, leaf	51·2	,,	50·2-52	,,
,, ,, outer part of leaf	50·7	,,		
Lard from belly	50·4	,,		
,, ,, intestines	49·0	,,		
,, ,, foot	...	...	44·8	,,
,, ,, ham	...	...	51·9-53	,,
,, ,, ,,	49·1[2]	Bömer	49·7-51·8[3]	Bömer
Beef tallow	49·0	Mansfeld		
Horse fat	53·7	,,		
Cocoa nut oil	35·5	,,		
Cotton seed oil	61	,,		

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[1] *Journ. Soc. Chem. Ind.* 1897, 88.

[2] Liquid Fatty Acids 42·8-42·2.

[3] Liquid Fatty Acids 43·1-44·7.

Deviations in the Oleo-refractometer (Amagat and Jean).

Kind of Fat or Oil.	"Degrees" in the Oleo-refractometer.	
	Fat.	Fatty Acids.
Lard, pure	−12·5	−30
Steam lard	−13	−30
Lard stearine	−10 to −11	
Beef tallow	−16; −17	−40
,, stearine	−34	
Veal ,, ...	−19	
Cotton seed oil	+20	+10
,, stearine	+25	+20
Sesamé oil	...	−18
Arachis oil	+5	
Lard with 10 per cent of beef tallow . .	−12	
,, ,, 20 ,, ,, ,, . .	−13	
,, ,, 50 ,, ,, ,, . .	−14	−33
,, ,, 5 ,, cotton seed oil . .	−10	
,, ,, 10 ,, ,, ,, . .	− 8	
,, ,, 15 ,, ,, ,, . .	− 7	
,, ,, 20 ,, ,, ,, . .	− 6	
,, ,, 25 ,, ,, ,, . .	− 5	
,, ,, 30 ,, ,, ,, . .	− 4	
,, ,, 40 ,, ,, ,, . .	0	
,, ,, 50 ,, ,, ,, . .	− 3	
,, ,, 5 ,, ,, stearine .	−11	
,, ,, 10 ,, ,, ,, .	− 7	
,, ,, 20 ,, ,, ,, .	− 4	
,, ,, 30 ,, ,, ,, .	− 3	
,, ,, 40 ,, ,, ,, .	− 2	
,, ,, 50 ,, ,, ,, .	+ 1	
Lard with 20 per cent of arachis oil . . .	− 8	−23
,, ,, 20 ,, sesamé ,, . . .	...	20
,, 40 per cent; beef tallow 40 per cent; cotton seed oil 20 per cent	...	−24
Steam lard 60 per cent; beef tallow 15 per cent; arachis oil 25 per cent . . .	− 8	
Lard 60 per cent; mutton tallow 25 per cent; arachis oil 15 per cent	−13	−22
Cocoa nut oil	−54	

From the following table, due to *Dupont*,[1] it will be seen that American lards show a smaller degree of deviation than European lards; if judged solely by the standard of European lards, they might be rashly condemned as containing cotton seed oil :—

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[1] *Journ. Soc. Chem. Ind.* 1895, 828.

[TABLE

American Lard.	Oleo-refractometer "Degrees."	Iodine Value.
From leaf	-11·5	58
,, back	-5	61
,, intestines	-7	62
,, head	-7	63
,, foot	-4	65
Gut lard	-11	60
Rancid lard	-7	63
,, lard	-6·5	64

The influence of rancidity on the refractometric constant is illustrated by the numbers given in the following table; they are contrasted with the *Reichert-Meissl* values (*Spaeth*):—

Deviation in the Butyro-refractometer calculated for 25° C.		Reichert-Meissl Values.
After 1 year.	After 3 years.	After 3 years.
59·35	62·60	...
60·21	62·30	4·3
60·49	62·45	9·36
57·71	58·75	1·32
60·35	62·70	...
61·35	63·10	...
58·14	63·1	3·74

Whereas adulteration with vegetable oils and fats can be detected with certainty by the phytosteryl acetate test (p. 373), the recognition of beef tallow, oleomargarine, and beef stearine presents considerable difficulties, the more so as small quantities, down to 5 per cent, repay the cost entailed in the mixing.

I shall indicate in the following lines special methods for the detection of the more important adulterants.

Vegetable Oils

The phospho-molybdic acid test (p. 330) has been recommended by several observers as a method to indicate the presence of vegetable oils in lard with certainty. The writer has, however, shown[1] that a slightly rancid lard also reduces the reagent, and, furthermore, that an admixture of less than 15 per cent of cotton seed oil with pure lard cannot be thus detected. This test can therefore only be admitted as a preliminary one. The writer's experiments have been repeated and confirmed by *Samelson* and *Tennille*.

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[1] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1894, 619.

The surest proof of the presence of vegetable oils is obtained by the phytosteryl acetate test. Even 1-2 per cent of vegetable oils may thus be detected. Since this test is somewhat cumbersome, and will therefore only be resorted to when other methods fail to give a decisive answer, the determination of the iodine value of the sample and of its fatty acids should be looked upon as the readiest means of furnishing preliminary information.

If the presence of a vegetable oil has been indicated by an abnormally high iodine value, one of the following four oils should be specially looked for:—Arachis oil, sesamé oil, cotton seed oil (cotton seed stearine), maize oil.

Arachis Oil.—*Renard's* test should give a positive result; the amount of arachis oil present can be approximately calculated from the weight of the crude arachidic acid obtainable.

Sesamé Oil.—This would be detected readily by *Baudouin's* reaction.

Cotton Seed Oil (Stearine).—For the preliminary detection of cotton seed oil or cotton seed stearine in lard the colour reactions described (p. 534) may be employed. The most useful amongst these tests is the *Halphen* test. It has been stated already that an over-estimation of the indications furnished by this test may lead to grave errors. If a positive *Halphen* colour reaction has been obtained, the presumption only is raised that the sample of lard is adulterated with cotton seed oil. It must, however, be distinctly understood that no more than a presumption is raised, for neither does a positive test indicate with certainty that cotton seed oil is present, nor does a negative test prove the absence of cotton seed oil. For, as pointed out already, the colouring matter contained in cotton seed passes into the lard from hogs fed on cotton cake. This has been placed beyond doubt by several observers (*Langfurth*,[1] *Soltsien*,[2] *Fulmer*.[3]) Hence it would be entirely misleading to conclude from a positive *Halphen* reaction that cotton seed oil is present, and more erroneous still would it be to judge from the depth of the tint as to the approximate amount of cotton seed oil present. I lay stress on this, as attempts have been made to convert the *Halphen* test into a colorimetric quantitative reaction. *Langfurth* has shown that lard obtained from a hog fed experimentally on cotton cake gave as strong a coloration as was obtained by a mixture of lard with 30 per cent of cotton seed oil; he therefore rightly points out that the quantity of lard obtained from a single hog fed on cotton cake would be quite sufficient to so contaminate a tank-car of lard, that the mixture would still give a very distinct coloration in the *Halphen* test.

If therefore on testing a specimen of lard, a coloration has been obtained, further tests must be applied, especially the phytosteryl acetate test. If employed with due precaution, the *Halphen* test will be found a very useful preliminary test, especially in those cases where a large number of samples must be tested rapidly.

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[1] *Zeit. angew. Chem.* 1901, 685.

[2] *Zeit. öffentl. Chem.* 1901, 140.

[3] *Journ. Amer. Chem. Soc.* 1902, 1148.

As has been pointed out already, a negative *Halphen* test does not prove the absence of cotton seed oil, since heated cotton seed oils do not give a coloration with *Halphen's* reagent.

If the *Halphen* test give a negative result, the **nitric acid** test may be usefully applied as a further preliminary test, for, as I have shown above (p. 534), heated cotton seed oil still gives a brown coloration. But it must be remembered that lards from hogs fed on cotton cake also give the brown coloration. Still, the absence of a brown coloration may indicate the absence of considerable quantities of cotton seed oil.

The reduction of silver nitrate by any of the tests described (p. 535) by no means proves the presence of cotton seed oil. Lard obtained from hogs fed on cotton cake reduces the *Bechi* reagent completely (*Langfurth*). Even lards obtained from normally fed hogs occasionally reduce silver nitrate solution (*Wesson*, *Mariani*,[1] *Bevan*[2]).

To illustrate the foregoing remarks by an example, I give a short summary of an examination (carried out in my laboratory) of a specimen of lard which gave the following indications:—

Iodine Value of Lard	76·5
Iodine Value of the Liquid Fatty Acids	115·5
Unsaponifiable Matter	0·35 per cent.

Halphen test, slight coloration, such as would be indicated by a lard containing an admixture of about 6 per cent of cotton seed oil.

The high iodine value in conjunction with the positive *Halphen* test raised the presumption that this lard was adulterated with cotton seed oil. Hence the examination by the phytosteryl acetate test had to be carried out.

A preliminary microscopic examination of the unsaponifiable matter (cp. chap. ix. (*a*)), showed that phytosterol was absent, the characteristic crystals of cholesterol only having been obtained. The unsaponifiable matter was then examined by the phytosteryl acetate test with the following result:—

Crystals.	Melting Point. °C.
2nd Crop	113
3rd Crop	114-114·5
4th Crop	115
5th Crop	113-114

From these results it became evident that the lard was free from cotton seed oil or any other vegetable oil.

As lard gives a liquid product with **sulphur chloride**, which is soluble in carbon bisulphide, cotton seed oil may also be detected qualitatively by means of that reagent (*B. Warren; Jones*[3]). In the

[1] *Journ. Chem. Soc.* 1894. Abstr. II. 75.

[2] *Analyst*, 1894, 88.

[3] *Analyst*, 1888, 170.

presence of cotton seed oil a hard mass partly insoluble in carbon bisulphide is produced.

I have tried this method and found it very useful indeed. My observations are given in the following table :—

Mixtures of Lard and Cotton Seed Oil (*Lewkowitsch*)

5 grms. of fat dissolved in 2 c.c. CS_2, added 2 c.c. S_2Cl_2, and placed on the water-bath

Lard. Per cent.	Cotton Seed Oil. Per cent.		Solubility of Product in Carbon Bisulphide.
100	0	No reaction	Completely soluble
90	10	Thickens after 35 minutes	,, ,,
80	20	,, ,, 30 ,,	52 per cent ,,
70	30	,, ,, 26 ,,	39·6 ,, ,,
60	40	,, ,, 18 ,,	34·8 ,, ,,
50	50	Solid after 10 ,,	37·4 ,, ,,
40	60	,, ,, 8 ,,	30·6 ,, ,,
30	70	,, ,, 7 ,,	32·6 ,, ,,
20	80	,, ,, 6 ,,	30·0 ,, ,,
10	90	,, ,, 4 ,,	28·4 ,, ,,
0	100	,, ,, 3 ,,	24 ,, ,,

It is advisable to test the sample side by side with pure lard, or better still, with mixtures of lard and cotton seed oil (or cotton seed stearine) prepared in a similar fashion to that illustrated by the table.

Maize Oil.—If arachis and sesamé oils are absent, too high an iodine value can only be due to cotton seed oil or maize oil. The solidifying point of the mixed fatty acids would in this case lead to a decision if only one oil be present. If both are present, this method breaks down. With regard to the "sitosterol test" (p. 514).

Cocoa nut oil or **palm kernel oil** will be recognised by the high saponification value, and especially by the definite Reichert value of the sample. In doubtful cases the phytosteryl acetate test—provided vegetable oils be absent—will lead to conclusive evidence. If the iodine value of the lard or of the mixed fatty acids is abnormally low, then the presence of cocoa nut oil or palm kernel oil may be suspected.

Animal Fats

The detection of **tallow** and (or) **beef stearine** in lard is a difficult problem, and can only be solved successfully, in the present state of our knowledge, by strict comparison with samples of pure lard and of lard mixed with known proportions of the adulterant suspected. This problem is rendered all the more difficult as American steam lard behaves very differently from European home rendered lard (*Goske*).

Beef stearine, when present in quantities of at least 10 per cent, may be detected, according to *Leopold Meyer*, by melting a somewhat large quantity in a capacious beaker and allowing to stand at a temperature of 31° to 32° C. for 36 hours. Pure lard crystallises homogeneously from the bottom of the vessel upwards, whereas presence of beef stearine is said to be indicated by the appearance of crystals resembling cauliflower. This can obviously only be used as a preliminary test.

Belfield dissolves the sample in ether, and examines the crystals which separate from the ethereal solution under the microscope. Forty drops of the melted lard are dissolved in 10 c.c. of ether in a test-tube and allowed to cool (*Pattinson* [1]). Should no crystals form, the cork is removed from the tube and a loose plug of cotton-wool substituted, when crystals will be obtained by the spontaneous evaporation of the ether. If the crystals have been formed too rapidly it is best to redissolve them by addition of more ether. Some of the crystals are then placed on an object-glass and examined microscopically. Crystals from pure lard usually form oblong plates—either singly or in bunches—and have oblique terminals, whereas those from beef tallow form curved tufts of very thin needles somewhat of the shape of an "*f*."

I have examined microscopically the crystals obtainable from specimens of leaf lard, lard from the loin, lard from the shoulder, and lard from the back, all of which were rendered in the laboratory. Forty drops of the melted fat were dissolved in 10 c.c. of ether, and were allowed to crystallise under exactly the same conditions in corked test tubes.

In the case of leaf lard, bunches of crystals were obtained, which under a low power of magnification appeared as needles, but under a higher power were distinctly discernible as plates.

The lard from the shoulder yielded some isolated plates, but mostly bunches, radiating from a centre point in all directions, thus forming a whole circle or parts thereof. But there also appeared bunches of crystals which were very similar to tallow crystals; only under a high power of magnification they showed the chisel-shaped ends characteristic of lard crystals. Small bunches of crystals were, however, noticed which were distinguishable from beef tallow crystals. Moreover, in various preparations the plates did not even predominate over those crystals which appeared to be most like beef crystals.

The lard from the loin showed many distinct straight plates with chisel-shaped ends characteristic of lard crystals. These were even noticeable in the thickest plates which at first appeared like beef crystals. A number of plates were observed, especially amongst those in the bunches, which were curved, and as they had the shape of distinct plates, would appear to represent the transition form of plates (from lard) to needles (from tallow).

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[1] *Journ. Soc. Chem. Ind.* 1889, 30.

The lard from the back, which took the longest time to crystallise, (no doubt because it was the softest lard), showed distinct plates throughout, both as regards the isolated crystals, as also those heaped in bunches. The crystals from the back lard showed much longer plates than the crystals obtained from any other part. This is most likely due to the longer time required for crystallisation.

Mixtures of lard from the back fat with 5 to 10 per cent of tallow, I prepared, show distinct plates of lard crystals side by side with distinct bunches, which, even under a magnification of 670, could not be recognised as having chisel-shaped ends. Still, it would be hazardous to pronounce a definite opinion on the strength of these microscopic indications.

Goske[1] stated at first that 5 per cent of beef fat, or 15 per cent of mutton fat (which does not crystallise so well), can be detected if the ethereal solution be allowed to crystallise at a temperature of 12°-13° C. But later he admits that the question becomes complicated if oleomargarine is substituted for beef stearine. Besides, German home-rendered lard does not yield the crystalline plates, crystallising as it does in needles which are not readily distinguishable from those yielded by beef stearine under the same conditions.

Stock[2] compares the crystals obtained from an ethereal solution with those from two standard sets of mixtures, the first consisting of pure lard melting at 34°-35° C., with 5, 10, 15, and 20 per cent of beef stearine melting at 56° C.; the second of pure lard, of melting point 39°-40° C., with 5, 10, 15, and 20 per cent of beef fat melting at 50° C. *Stock* proceeds as follows:—The melting point of the sample is determined first by the capillary tube method. Suppose the melting point be found at 34° C., then 3 c.c. of the melted fat are run into a graduated stoppered cylinder of 25 c.c. capacity, 21 c.c. of ether are added, and the fat dissolved at 20°-25° C. 3 c.c. of each of the first set of mixtures are treated in exactly the same way. The five cylinders are cooled down to 13° C., and allowed to remain at that temperature—particularly during the last hours—for twenty-four hours.

An approximate estimate as to the amount of the adulterant is arrived at by reading off the apparent volume of deposited crystals. The ether is then poured off as far as possible, and 10 c.c. of fresh ether at 13° C. is added in each case. The cylinders are again shaken, cooled as before, and the proportion of crystals read off. Finally, the contents of the cylinders are emptied into weighed shallow beakers, the ether drained off carefully, the mass allowed to dry for fifteen minutes at 10° C., and weighed. The weight obtained for the sample under examination is compared with the weight of crystals obtained from whichever of the standards comes nearest to it.

The second set of mixtures is used for samples with a higher melting point.

The actual presence of beef fat should then be proved by microscopical examination, using a 1-inch objective and the C eye-piece.

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[1] *Journ. Soc. Chem. Ind.* 1893, 469.

[2] *Analyst*, 1894, 2.

No sample of pure lard melting below 39° C. yielded more than 0·011 grm. of crystals under the above-stated conditions. A sample of the melting point 45·8° C. gave, however, 0·146 grm. of crystals.[1]

Cochran[2] uses fusel oil for the preliminary separation of stearine crystals, which he then examines by the *Belfield-Stock* method. He proceeds as follows:—2 c.c. of the melted fat are placed in a stoppered cylinder graduated for 25 c.c., and 22 c.c. of fusel oil are added. The contents of the cylinder are slightly warmed to effect complete solution, and gradually allowed to cool to 16°-17° C., at which temperature they are kept for two to three hours. The deposited crystals are filtered off, dissolved in ether, allowed to crystallise out as described above, and finally subjected to microscopical examination. *Cochran* claims that smaller proportions of beef fat can thus be detected than by the above described methods. Thus lard adulterated with 10 per cent of beef fat showed far more beef stearine than lard stearine crystals, whereas from a mixture containing 20 per cent of beef fat no lard crystals were obtained. Preliminary information is said to be gained by noting the volume of the crystals deposited from the fusel oil; beef fat gave 16 c.c. of deposit, pure lard only 4 c.c., whereas in the case of "oleostearine" the crystals filled the tube up to the level of the liquid.

In the present state of our knowledge,[3] *Stock's* modification of *Belfield's* method must be considered the best. Unfortunately, the form of crystals obtained from "softer" lards differs from those obtained from harder ones. As has been pointed out already, this is confirmed by *Hehner* and *Mitchell*[4] who state that the "soft lards" yield nothing but broad plates with pronounced chisel-shaped ends, whereas from the harder ones bunches of more pointed, though still chisel-edged, needles crystallise. On being repeatedly recrystallised from ether they become more and more needle-like, approaching the form of beef stearine crystals, until they become undistinguishable from them.

In the second edition of this work (1898, p. 584) I suggested the determination of stearic acid in the saturated fatty acids of the sample as a means of detecting tallow in lard, since at that time the highest percentages of stearic acid found in lard varied from 6 to 16 per cent; and I expressed the opinion that the combination of the stearic acid and iodine tests would lead to decisive results. Since, however, *Hehner*[5] has obtained 24·91 per cent of stearic acid from a specimen of lard absorbing 45·6 per cent of iodine, the suggested method will not lead to decisive results.

Hence, the *Belfield-Stock* test must be used with great circum-

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[1] For Gladding's *modus operandi*, cp. *Journ. Soc. Chem. Ind.* 1896, 560.

[2] *Journ. Soc. Chem. Ind.* 1898, 74.

[3] A curious method to detect and determine the quantity of beef fat in lard is proposed by Balló, viz. to measure the amount of air enclosed in the melted fat: pure lard on solidifying is stated not to enclose any air, whereas pure beef fat encloses air (100 grms. about 6·5 to 8·8 c.c. Balló is of the opinion that even 3 per cent of beef fat may be thus detected (*Journ. Soc. Chem. Ind.* 1897, 764).

[4] *Analyst*, 1896, 328.

[5] *Ibid.* 1902, 248.

spection, and only when vegetable oils have been shown to be present (by the phytosteryl acetate test) the appearance of beef crystals can be accepted as affording evidence of the presence of tallow (*Hehner*).

Since mixed glycerides have been discovered in both lard and tallow, the likelihood must be taken into consideration that the same mixed glycerides may occur in both. Therefore, in the present state of our knowledge all evidence derived by recrystallising fats from solutions and examining the crystals must be accepted with reserve.

Since *Kreis* and *Hafner* have detected daturodistearin in lard (p. 16), whereas hitherto only palmito-distearin and oleopalmitostearin have been obtained from tallow, the isolation of *daturic* acid may be suggested as the direction in which further work should branch out.

A further line of research may be found in the following suggestion:—

Since lard contains, as has been shown above, p. 780, considerable amounts of myristic and lauric acids, whereas the saturated acids in tallow consist of palmitic and stearic acids only, the application of the lithium salt method (p. 353) may in doubtful cases afford some valuable information. True, vegetable oils, such as cocoanut oil, may interfere with the indications furnished by the lithium acetate method, but their presence would be detected by the phytosteryl acetate test.

It should be pointed out that I have not tested the value of these suggestions by experiments.

On subjecting lard to hydraulic pressure (see "Demargarinating processes," p. 444) lard stearine and lard oil are obtained.

Lard stearine is used in the United States in the manufacture of margarine ("oleomargarine"). Of course, only the purest and sweetest lard stearine can be employed for edible purposes. Lard stearine which does not fulfil this demand, such as the stearine obtained from prime steam lard, is used as candle material. A sample of such material examined in my laboratory had the melting point 125° F. = 51·7° C.

Lard oil.—French—*Huile de lard*, German—*Schmalzoel*, Italian—*Olio di lardo*, if obtained from the best neutral lard, is used as an ingredient in the manufacture of margarine, etc. Lower qualities are employed as high-class burning and lubricating oils.

According to the pressure and the temperature employed in the process of separating the liquid from the solid portion the solidifying point of lard oil will vary, so that some specimens will deposit "stearine" at the ordinary temperature, or even solidify completely at 10°-12° C., whereas others do not deposit any crystals unless cooled to the freezing point. Hence the usual characteristics such as the specific gravities, and especially the iodine values of different lard oils, will vary considerably as evidenced by the numbers contained in the following table:—

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[1] *Analyst*, 1902, 248.

Characteristics of Lard Oil.

Specific Gravity.			Saponification Value.		Iodine Value.		Reichert-Meissl Value.		Maumené Test.		Butyro-refractometer.	
At °C.		Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	° C.	Observer.	At 40° C.	Observer.
15	0·916	Duyk[1]	193	Duyk	73	Duyk	0	Duyk	47	Duyk	41	Duyk
15·5	0·915	Allen			67-79[3]	Schweitzer and Lungwitz						
18	0·9137	Long										
20	0·9122	,,			80-82	Dupont						
25	0·9088	,,			69·7-75·9	Tolman and Munson						
30	0·9053	,,			70-75[2]	Voigtländer						
35	0·9019	,,			88[3]	,,						
100	0·8626	Duyk										

The Iodine Value of the Liquid Fatty Acids[4]

94·0-95·8.

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[1] *Bull. Assoc. Belge des Chim.* 1901, 590.

[2] European.

[3] American.

[4] *Journ. Amer. Chem. Soc.* 1903, 966.

In the elaidin test, lard oil behaves very much like olive oil.

Pure lard oil should be free from fatty acids. Adulterants, such as mineral oils or vegetable oils, are detected by the quantitative reactions, and the methods described above. Fish oils in lard oil intended for lubricating purposes are best detected by isolating the hexabromides of the liquid fatty acids.

Tolman and *Munson*[1] found in a number of lard oils from 18·9 to 26·7 per cent of solid fatty acids by the lead-salt-ether method.

BEEF MARROW FAT

French—*Graisse de moëlle de bœuf.* German—*Rindermarkfett.*
Italian—*Grasso di medollo di bove.*

For tables of constants see p. 804.

Beef marrow fat is the fat from the marrow bones of cattle.

Medullic acid, stated by *Eylerts* to occur in beef marrow, is, according to *Thümmel*, a mixture of palmitic and stearic acids.

A specimen of freshly rendered marrow fat had the acid value 1·6, and a specimen eight months old 1·9 (*Zink*).

Beef marrow fat is used in pharmacy and for making pomades.

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[1] *Journ. Amer. Chem. Soc.* 1903, 966.

[TABLE

Physical and Chemical Constants of Beef Marrow Fat

Specific Gravity.		Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Reichert Value.	
At 15° C.	Observer.	° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.
0·9311-0·938	Zink	31-29	Zink	37-45[1]	Zink	199·6 195·8-198·1	Lewkowitsch Zink	55·4 39·2-50·9	Lewkowitsch Zink	1·1	Zink

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.		Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.	
At 15° C.	Observer.	° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
0·9300-0·9399	Zink	37·9-38[1] 40-39	Lewkowitsch Zink	45-46[2]	Zink	204·5	Zink	55·5	Lewkowitsch

[1] Titer Test.

[2] Capillary Tube Method.

BONE FAT

French—*Suif d'os.* German—*Knochenfett.*
Italian—*Grasso d'ossa.*

For tables of constants see p. 806.

Bone fat is obtained by two processes—(1) by boiling bones with hot water or by steaming; (2) by extracting bones with volatile solvents.

(1) If prepared from fresh bones by the first process, bone fat has a white to yellowish colour, a faint odour and taste, and its consistence is that of butter. Commercial bone fat, however, is usually recovered from old, sometimes putrid bones, and according to the age and state of rancidity of the bones, the bone fat may pass through all gradations, from white fat containing a few per cent of free fatty acids and an inconsiderable amount of impurities, through a slightly brownish less pleasantly smelling fat, to a dark brown mass of offensive odour, containing besides neutral fat large quantities of free fatty acids and lime soaps, formed by the action of fatty acids on the lime salts of the bones, and furthermore calcium salts of lactic acid and of lower fatty acids such as butyric, etc., which are the usual concomitants of rancidity.

By the boiling out process only half of the fat contained in the bones can be recovered. 4-5 per cent of bone fat can be thus recovered from bones containing 8-10 per cent.

Bone fat of this quality can be bleached, but only the best kinds will be likely to yield a good product. The higher the percentage of free fatty acids, the greater will be the difficulty in bleaching. In fact, products containing more than 50 per cent of free fatty acids cannot be bleached successfully.

(2) Bones that are no longer fresh are usually extracted with benzine (petroleum ether) in digesters under pressure, or in open apparatus. The method in which pressure is employed is the more dangerous one, and has not infrequently led to explosions. The advantage which this method offers is that practically the total amount of fat contained in the bones can be extracted, the actual yield depending on the nature of the solvent and the time during which the solvent acts on the bones, as also on the construction of the apparatus. That apparatus will be the best in which the volatile solvent is so successfully condensed that only a small amount of it is lost. The fat obtained by the extracting process is dark brown, and has a very penetrating, unpleasant smell. Besides a considerable amount of free fatty acids this fat contains lime soaps, calcium lactate, calcium butyrate, hydrocarbons from the petroleum ether, and colouring substances. This kind of fat cannot be bleached successfully, and even if some immediate improvement is obtained by bleaching, the colour, as also the unpleasant smell, will "revert" a short time after bleaching.

Physical and Chemical Constants of Bone Fat[1]

Specific Gravity.		Solidifying Point.		Melting Point.		Saponific. Value.		Iodine Value.	
At 15·5° C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
0·914-0·916	Allen	15 rising to 17	Schaedler	21-22	Schaedler	190·9	Valenta	46·3-49·6	Wilson
...	...	...	...	...	...	194-195[1]	Lewkowitsch	48-55·8	Valenta

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.		Neutralisation Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.	Mgrms. KOH.	Observer.
28	Hübl	30	Hübl	57·4[2]	Morawski and Demski	200	Valenta
...	...	...	...	55·7-57·3[3]			

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[1] Prepared by boiling out fresh bones.

[2] Crude fat.

[3] Refined fat.

Whereas the bone fat obtained by the first process can be used in soapmaking, the fat obtained by the second process is utterly unsuitable for soapmaking, and can only be worked up in candle works.

If a bone fat intended for soapmaking purposes contain a considerable amount of lime, the bone fat is best treated with dilute mineral acid.

The chemical composition of bone fat lies between that of marrow fat and tallow. Hence the valuation of bone fat is carried out in a similar manner to that of tallow. But a complication arises through the presence of calcium salts of higher fatty acids, and of calcium lactate and butyrate.

It has been pointed out already (p. 146) that the lime soaps tenaciously retain water, so that the direct determination of moisture may lead to erroneous results. With regard to impurities of a non-fatty nature, it should be borne in mind that different results are obtained according as the fat is extracted after previous drying as in the English or German method, or is extracted undried as in the French method. From dried bone fats most of the lime salts are dissolved by petroleum ether, whereas in the case of undried bone fats most of the soaps remain undissolved. The method employed should, therefore, be distinctly stated when returning the results of the analysis.

The errors inherent to the older methods are avoided by adopting the process proposed by *Shukoff* and *Schestakoff*:[1]—

Fatty Matter.—This is determined direct. Weigh off 10 grms. in a small conical flask, add 3 to 5 drops of strong hydrochloric acid, and warm on the water-bath for about 1 hour, agitating the contents of the flask from time to time, whereby the lime-soaps are decomposed. Then add 40 c.c. of petroleum ether, agitate to dissolve the fatty matter, and pour the solution carefully (leaving the few drops of acid at the bottom of the flask) through a tared filter into a second flask; wash two or three times with petroleum ether, and determine the fatty matter in the ethereal solution as described p. 150.

Impurities, organic and inorganic.—The dirt and the acid solution from the first flask are washed on to the tared filter, dried, and determined as described (p. 147); of course, lime and other inorganic substances are washed away in the acid solution.

Ash.—This is found by incinerating a fresh portion of the sample. The lime of the organic lime salts is thus converted into calcium carbonate; the amount of the latter may be ascertained by titrating the ash with standardised acid.

Moisture.—This is found by difference.

The fatty matter consists, of course, of the neutral fat and of the fatty acids which were originally contained in the bone fat, and of fatty acids liberated from the lime salts. It also contains unsaponifiable matter; amongst the latter *Shukoff* and *Schestakoff* found choles-

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[1] *Chem. Rev.* 1898, 6.

terol to the extent of from 0·2 to 0·6 per cent. The amount of the unsaponifiable—if required—is found by the method described p. 294.

The following table reproduces some analyses published by *Shukoff* and *Schestakoff*:—

Description of Bone Fat.	Fatty Matter.	Impurities.		Moisture by Difference.	Unsaponifiable Matter.	Titer Test.
		Organic.	Inorganic.			
	Per cent.	Per cent.		Per cent.	Per cent.	°C.
Russian—Petersburg .	98·65	0·15		1·20	1·80	39·9
,, .	99·00	0·15		0·85	0·82	39·9
,, .	99·10	0·10		0·80	0·52	40·2
Russian	99·15	0·10		0·75	0·50	42·5
,, ...	97·30	0·10	0·40	2·47	1·07	40·3
,, ...	96·60	0·05	0·50	3·58	1·12	39·1
,, from the South .	94·35	0·25	0·90	4·50	1·40	41·4
,, ,, .	92·45	0·30	0·70	6·55	1·20	40·9
,, ,, .	93·35	0·08	0·20	6·37	1·26	39·7
English—pale . .	98·20	0·25	0·75	1·42	0·56	39·3
,, "melted stuff"	97·04	0·30	0·15	2·15	...	39·8

The following two tables contain some analyses of bone fats. The first table is due to *Valenta*,[1] the second to *Troicky*[2]—

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[1] *Zeit. f. chem. Industrie*, 1887, 265; *Journ. Soc. Chem. Ind.* 1888, 219.

[2] *Chem. Zeit.* 1890, Rep. 239.

Bone Fat.	No.	Water. Per cent.	Fatty Acids. Per cent.	Free Fatty Acids. Per cent.	Melting Point of Fatty Acids. °C.	Neutralisation Value. Fatty Acids.	Iodine Value of Fatty Acids.	Ash. Per cent.	Remarks.
Extracted .	1	6·31	89·8	25·8	41·5	206	52·1	1·35	Very impure, nearly black, smell unpleasant.
,, .	2	2·20	93·7	...	42·3	204·5	50·9	1·85	Brown.
,, .	3	2·55	91·5	18·7	41·7	205	51·3	2·01	...
,, .	4	...	...	...	42·0	205	48	...	Fatty acids obtained from No. 1 by distillation.
,, .	5	17·0	93·5	26·5	41·5	200	51·3	1·3	Rather dark.
,, .	6	1·33	...	24·6	41·5	206·1	55·8	0·11	...
,, .	7	...	92·9	18·4	41·8	205·8	52·8	...	Very dark.
,, .	8	...	92·3	20·1	42·0	205	...	...	...
Boiled out	9	...	...	...	45·1	201	44·3	...	Fatty acids from marrow bones prepared in laboratory.
,, .	10	...	...	...	33·5	208·1	75	..	Fatty acids from horse marrow bones, prepared in laboratory.
,, .	11	2·05	90·4	14·8	41·5	207	53·5	...	...
,, .	12	3·08	90·7	21·9	41·7	206	52·8	...	...

No.	Description of Bone Fat.	Water.	Ash.	Fatty Acids.	Saponification Value.	Iodine Value.	Solidifying Point of Fatty Acids.	Oleic Acid.	Stearic Acid.
		Per cent.	Per cent.	Per cent.			°C.	Per cent.	Per cent.
1	Boiled out . .	1·20	0·31	93·20	187·0	57·2	39·0	59·18	34·02
2	,, . .	0·47	0·94	94·40	194·3	56·0	40·2	58·69	35·71
3	Extracted . .	0·58	0·56	94·12	193·8	52·0	40·9	54·34	39·78
4	Boiled out, Russian	0·84	2·40	86·10	172·0	50·3	42·65	48·08	38·02
5	Extracted, ,, .	0·78	1·25	91·30	188·7	51·5	40·75	52·20	39·10
6	,, . .	0·85	1·76	91·00	181·0	54·8	40·0	55·36	35·64
7	,, . .	1·82	1·52	92·40	185·6	55·8	40·1	57·24	35·16
8	,, . .	0·91	1·06	92·85	187·0	55·2	40·9	56·90	35·95
9	Boiled out, from horse bones	1·52	1·82	91·50	184·0	62·7	36·1	63·69	27·81

TALLOW [BEEF TALLOW. MUTTON TALLOW.]

In commerce a distinction is made between *beef tallow* and *mutton tallow.* The former is obtained from oxen, cows, and calves; the latter from sheep and goats. This distinction is, broadly speaking, supported by chemical differences in the composition of the triglycerides, mutton tallow being as a rule richer in stearin than beef tallow.

The quality—especially the hardness—of tallow depends on the breed and the age of the animal, and to some extent on the food. The fat from the male beast is generally harder than that obtained from the female. Animals fed on grass yield a harder fat than those fed with oilcakes; brewery refuse especially produces soft tallow. Hence we have all gradations, from the hard South American beef tallow to home melt tallow of somewhat softish consistence.

The rough fat is delivered with the adhering tissue, etc., to the tallow-melters, and is rendered at a temperature of about 100° C. or above, as has been described already, p. 443.

The fats from different parts of the carcass, although of unequal value, are not kept separate, unless the fat be intended for the manufacture of oleomargarine. In that case the more valuable kidney fat ("suet") and bowel fat ("midgerum fat") [French, *suif en branches* or *en rames;* German, *Rohkern*] is dealt with separately and not mixed with the caul- (or kell-, i.e. *omentum*) fat [French, *dégraisse;* German, *Rohausschnitt*].

By melting this selected fat at low temperatures—not exceeding 50° C.—the "premier jus" is obtained (cp. chap. xv. "Margarine").

Commercial brands of tallow are therefore—

(1) Rendered tallow, which contains all the fat from the carcass.
(2) Pressed tallow. Tallow stearine.
(3) "Premier jus."

The imported tallows, such as Australian, South American, North American, are, of course, tallows of the first kind. Tallow is sold according to its titer (titre), and according to colour (good colour, no colour, etc.) The titer tests of the commercial brands most frequently met with have been given already (p. 182).

Like lard, tallow is frequently expressed in hydraulic presses, when "*tallow stearine*" and "*tallow oil*" are obtained.

Tallow oil (French, *huile de suif;* German, *Talgoel*) is liquid or semi-solid according to the temperature at which it has been expressed. Tallow oil is chiefly used in admixture with mineral oils as lubricating oil. Its solidifying and melting points, as also its iodine values, naturally vary according to the conditions under which the tallow has been expressed. Hence the following characteristics have only limited application:[1]—

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[1] Due to Gill and Rowe, *Journ. Amer. Chem. Soc.* 1902, xxiv. 466.

Specific Gravity at 100° C.	Titer Test. °C.	Iodine Value.	Iodine Value Mixed Fatty Acids.	Maumené Test. °C.
0·794	34·5-37·5	55·8-56·7	54·6-57	35·0

BEEF TALLOW

French—*Suif de bœuf.* German—*Rindstalg.*
Italian—*Sego di bove.*

For tables of constants see p. 814.

Beef tallow when freshly rendered is nearly white, free from disagreeable odour, and almost tasteless. In commerce it is sold as "Home melt beef tallow." Imported tallow passes through all gradations, from slightly yellowish tallow (Australian), through darker yellow (North American, South American) to the off-coloured lowest grades (North American, Australian—no colour).

Tallow was until recently considered to consist exclusively of the glycerides of palmitic, stearic, and oleic acids. The amount of olein used to be calculated from the iodine value. Thus a tallow absorbing 43 per cent of iodine was looked upon as containing 50 per cent of olein. It is not unlikely that owing to the influence of vegetable fats given with the food (oilcakes, etc.) less saturated acids than oleic acid may be found. *Farnsteiner* claims to have obtained small quantities of linolenic hexabromide, pointing to the presence of small quantities of linolenic acid in beef tallow.[1] Recent researches have further shown that it is no longer permissible to adopt the view that palmitin, stearin, and olein are contained as simple triglycerides in tallow, as the following mixed glycerides have been isolated by crystallising tallow from solvents:—oleodipalmitin, stearodipalmitin, oleopalmitostearin, palmitodistearin (see p. 15).

The examination of tallow by the lithium salt method for small quantities of myristic acid is desirable.

The proportions of palmitin, stearin, and olein vary in the fats rendered from different parts of the same beast. *Leopold Mayer*[2] has examined the fats obtained from different parts of the body of an Hungarian ox, three years old, with the result contained in the following table:—

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[1] *Zeit. f. Unters. Nahrungs. u. Genussmittel*, 1899, 25.

[2] Wagner's *Jahresbericht*, 1880, 844.

[TABLE

Tallow from	Fat.				Fatty Acids.				
	Solidifying Point (Pohl's method).	Melting Point (Pohl's method).	Saponification Value.	Hehner Value.	Solidifying Point (Pohl's method).	Melting Point (Pohl's method).	Neutralisation Value.	'Stearic Acid,'[1] Solidifying Point 54·8° C.	Oleic Acid, Solidifying Point 5·4° C.
	°C.	°C.			°C.	°C.		Per cent.	Per cent.
Intestines .	35·0	50·0	196·2	95·7	44·6	47·5	201·6	51·7	48·3
Lungs . .	38·0	49·3	196·4	95·4	44·4	47·3	204·1	51·1	48·9
Caul . .	34·5	49·6	193·0	95·8	43·8	47·1	203·0	49·0	51·0
Heart . .	36·0	49·5	196·2	96·0	43·4	46·4	200·3	47·5	52·5
Neck . .	31·0	47·1	196·8	95·9	40·4	43·9	203·6	38·2	61·8
Groins . .	35·0	42·5	198·3	95·4	38·6	41·1	199·6	33·4	66·8

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[1] In the commercial sense of the term, *i.e.* mixed stearic and palmitic acids.

Physical and Chemical Constants of Beef Tallow

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Reichert Value.	Hehner Value.		Thermal Test. Heat of Bromination.		Refractive Index.	
At ° C.		Observer.	° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Per cent.	Observer.	° C.	Observer.	At 60° C.	Observer.
15	0·943-0·952	Dieterich	35-27 Temperature rises a few degrees without, however, remaining constant.	Rüdorff	45-46; 42-43, not below 40	Wolkenhaar	195·7-200	Filsinger	40	Hübl	0·25	95·6	Bensemann	6·1[3]	Archbutt	1·4510	Thoerner
50 (water 15·5=1)	0·8950	Allen							43·3-44	Wilson							
					47·6-48·5	Dieterich	193·2-198	Köttstorfer Deering L. Mayer	35·4-36·4	Filsinger		95·4-96	L. Mayer	6·7-7·2[4]	,,		
98 (water 15·5=1)	0·8626	,,			43·5-45	Rüdorff			35·6-38·9	Dieterich						Butyro refractometer.	
									45·2[1]	Wallenstein and Finck							
100 (water 15=1)	0·860-0·861	Wolkenhaar							38·3[2]	,,						At 40° C.	Observer.
									38-40	Thoerner							
100 (water 15=1)	0·860	Koenigs							41-47·5	Lewkowitsch						49	Mansfeld

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.		Solidifying Point.		Melting Point.		Neutralisation Value.		Mean Molecular Weight.		Iodine Value.		Refractive Index.	
At 100° C. (water at 100=1)	Observer.	° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.		Observer.	Per cent.	Observer.	At 60° C.	Observer.
0·8698	Archbutt	Titer Test.		43-44 and 46-47	Bensemann	197·2	Lewkowitsch	270-285	A. Wright	41·3	Williams	1·4375	Thoerner.
						201·6	Thoerner	284·5	Lewkowitsch	25·9-32·8	Morawski and Demski	Oleo-refractometer.	
		43·5-45	Dalican	45	Hübl					Iodine Value of the Liquid Fatty Acids.		"Degrees."	Observer.
		44·5	De Schepper and Geitel							92·4[1]	Wallenstein and Finck	−40	Jean
		43	Hübl							92·2[2]	,,		
		Cp. p. 182	Lewkowitsch										

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[1] Australian.

[2] Berlin town tallow.

[3] American beef.

[4] Home-refined.

The ratio of stearin to palmitin is about 1 : 1.

According to *Wallenstein*[1] a sample of tallow stearine had the following composition:—

Olein	21·4 per cent.
Stearin	65·4 ,, ,,
Palmitin	13·2 ,, ,,

More definite information as to the amount of stearic acid and its proportion to palmitic acid is obtained by *Hehner* and *Mitchell's* method of determining stearic acid (chap. viii. p. 354). In the following table some results obtained by this method are collated:—

	Iodine Number.	Stearic Acid in Fatty Acids.	Observer.
		Per cent.	
Tallow, several samples	...	21-22	Lewkowitsch
Beef stearine . .	2·0	50·19-51·05	Hehner & Mitchell[2]

The amount of free fatty acids in tallow varies considerably with the state of purity. In freshly rendered tallows the proportion of free fatty acids is negligible and rarely exceeds 0·5 per cent; in commercial samples the percentage of free fatty acids may rise to 25 per cent and even more. Hence the acetyl values shown by tallows of different states of purity will also vary. Thus *Lewkowitsch* found acetyl values varying from 2·7 to 8·6 in different brands of tallow. It need hardly be repeated (cp. p. 276) that these acetyl values do not indicate the presence of hydroxylated acids. In this connection it may be pointed out that *Fahrion*[3] found in a specimen of tallow 0·13 per cent of "oxidised" acid.

Valuation of Tallow.—The value of tallow is determined, apart from its colour, by the solidifying point ("titer") of its fatty acids. The higher the titer the more valuable is the tallow for the purposes of the candlemaker and soapmaker. The following empirical table compiled by *Dalican* is still used in a number of candle-works for an approximate estimation of the yield of commercial stearic acid from tallows having the solidifying point recorded in the first column of the table:—

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[1] *Journn. Soc. Chem. Ind.* 1893, 54.

[2] *Analyst*, 1899, 319.

[3] *Zeit. angew. Chem.* 1898, 784.

[TABLE

Solidifying Point. Titer Test.	Commercial Stearic Acid.	Oleic Acid.
C.	Per cent.	Per cent.
35	25·20	69·80
35·5	26·40	68·60
36	27·30	67·70
36·5	28·75	66·25
37	29·80	65·20
37·5	30·60	64·40
38	31·25	63·75
38·5	32·15	62·85
39	33·44	61·55
39·5	34·30	60·80
40	35·15	59·85
40·5	36·10	58·90
41	38·00	57·00
41·5	38·95	56·05
42	39·90	55·10
42·5	42·75	52·27
43	43·70	51·30
43·5	44·65	50·35
44	47·50	47·50
44·5	49·40	45·60
45	51·30	43·70
45·5	52·25	42·75
46	53·20	41·80
46·5	55·10	39·90
47	57·95	37·05
47·5	58·90	36·10
48	61·75	33·25
48·5	66·50	28·50
49	71·25	23·75
49·5	72·20	22·80
50	75·05	19·95
50·5	77·10	17·90
51	79·50	15·50
51·5	81·90	13·10
52	84·00	11·00
52·5	88·30	6·70
53	92·10	2·90

Tallows of a lower titer than 44° are unprofitable to the candle-maker, and are therefore chiefly employed for soap-making.

A large amount of **free fatty acids** depreciates the value of a tallow considerably, as the fatty acids obtained from such tallow in the lime saponification process turn out dark; also soap made from such tallow has an inferior colour ("foxy"). Nor can such tallow be used for lubricating purposes.

Water may be determined in the usual manner. *H. Norman Tate*[1] heats 50 grams in a porcelain crucible or silver crucible to 130° C. and keeps thereat until bubbles cease to be given up.

Adulterants in tallow are easily detected by means of the quantitative reactions. If required the phytosteryl acetate test may be applied for the detection of vegetable oils and fats. It must, however, be added that at present tallow is but rarely

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[1] The examination of tallow, Liverpool, 1888.

adulterated.[1] Home tallow is sometimes adulterated with *distilled grease stearine.*

This "stearine" is obtained by distilling "recovered grease," and expressing the solid portion of it; it consists chiefly (chap. xvi.) of stearic acid, iso-oleic acid, and small quantities of cholesterol and isocholesterol.[2] A tallow thus adulterated has a peculiar smell, a high acid value, and somewhat high amount of unsaponifiable matter. If the unsaponifiable be boiled with acetic anhydride and concentrated sulphuric acid a green fluorescence[3] would point to the presence of isocholesterol and, inferentially, to distilled grease stearine.

The fatty acids obtained from tallow thus adulterated turn yellow after a few days, and exhibit the peculiar smell characteristic of wool fat and its derivatives.

A high acid value may also be due to admixture with stearic acid ("cotton stearine") from cotton seed mucilage (chap. xvi.); in that case, of course, no isocholesterol reaction will be obtained, but the acid value and the amount of unsaponifiable matter will be found high.

Goat's tallow, sold in commerce as mutton tallow, is considered by candle-makers as an adulterant. Although such tallow has a high melting point it is not suitable for candles, owing to its fatty acids not crystallising readily, but solidifying to an amorphous mass, from which it is difficult to remove the imprisoned oleic acid. The candles prepared in the ordinary way from goat's tallow are of low quality, do not possess the metallic ring of first-class candles, and easily become discoloured through their retaining persistently oleic acid. The detection of goat's tallow is difficult; the surest indication is given by the smell of the sample (*Chevreul's* "acide hircique").

A mixture of 70 parts of goat's tallow and 30 parts of cotton seed oil has been sold, according to *Mayer*, as beef tallow. Neither the solidifying point of the fatty acids nor the iodine value of this fat revealed the fraud. In a case of this kind recourse must therefore be had to the determination of the iodine value of the liquid fatty acids, and the presence of cotton seed oil must be confirmed by the phytosteryl acetate test.

MUTTON TALLOW

French—*Suif de Mouton.* German—*Hammeltalg.*
Italian—*Sego di Montone.*

For tables of constants see pp. 819, 820.

Mutton tallow very much resembles beef tallow; it is frequently sold mixed with the latter as "mixed tallow." It is, as a rule, harder

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[1] In Germany paraffin oil is used by the custom-house officers for "denaturing" tallow if caustic soda be objected to.

[2] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1892, 142.

[3] *Ibid.* 1892, 144.

than beef tallow, and consequently its solidifying and melting points, as also those of its fatty acids, are higher. Mutton tallow is also more liable to turn rancid than beef tallow. For this reason it cannot be used in the manufacture of first-class butter-substitutes or high-class toilet soaps.

The fat rendered from various parts of two sheep gave, according to *Moser*,[1] the following results :—

Fat from	Fat.			Fatty Acids.	
	Solidifying Point.	Melting Point.	Saponification Value.	Solidifying Point.	Melting Point.
	°C.	°C.		°C.	°C.
Kidneys . . .	40·7-40·9	54·0-55·0	194·8-195·2	51·9-51·9	56·2-56·5
Caul and intestines .	39·2-39·7	52·0-52·9	194·6-194·8	50·4-50 6	54·9-55 8
Adipose tissue .	34·1-34·9	49·5-49·6	194·2-194·4	43·7-46·2	50·7-51·1

Very instructive is the information contained in the following table, due to *Hehner* and *Mitchell*;[2] the different specimens of fat were taken from a Scotch sheep eighteen months old :—

Fat from	Iodine Value.	Melting Point of Fatty Acids.	Stearic Acid.
	Per cent.	°C.	Per cent.
Kidneys . .	48·16	45·6	26·2-27·7
Back . .	61·3	41·4	24·8
Neck . .	48·6	42·2	16·4
Breast . .	58·2	33·8	About 1
Ham . .	50·6	40·8	No deposit after two days.

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[1] *Bericht der Thätigkeit der Landw. Versuchsstation. Wien*, 1882, 1883.

[2] *Analyst*, 1896, 327.

[TABLE

Physical and Chemical Constants of Mutton Tallow

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.
15	0·937-0·953	Dieterich	36-32 rising several degrees	Rüdorf	47-49	Dieterich	192-195·2	Thoerner
100	0·860	Koenigs			46·5-47·4	Rüdorf		
"	0·858	Thoerner	40-41	Thoerner	44-45	Thoerner		

Physical and Chemical Constants of Mutton Tallow—continued

Iodine Value.		Hehner Value.		Thermal Test.		Refractive Index.	
				Heat of Bromination.			
Per cent.	Observer.	Per cent.	Observer.	°C.	Observer.	At 60° C.	Observer.
35·2-46·2	Wilson	95·54	Bensemann	8·1 [1]	Hehner and Mitchell	1·4501	Thoerner
34·8-37·7	Dieterich			7·6 [2]	" "		
32·7	Thoerner			7·55 [3]	Archbutt		
43-44	"			8·9 [4]	"		
38·6	Wallenstein and Finck						

[1] From kidney. [2] From flare. [3] Australian mutton. [4] Home refined.

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Neutralisation Value.		Iodine Value.		Refractive Index.	
°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	At 60° C.	Observer.
41	Thoerner	49-50 and 53-54	Bensemann	210	Thoerner	34·8	Thoerner	1·4374	Thoerner
39	,,	49	Thoerner						
Titer Test.		46-47	,,			Iodine Value of the Liquid Fatty Acids.			
45-46 also	Dalican					92·7	Wallenstein and Finck		
43·2									
46·1	de Schepper and Geitel								
See p. 182.	Lewkowitsch								

BUTTER FAT

French—*Beurre de vache.* German—*Butterfett.*
Italian—*Burro di vacca.*

Butter fat or milk fat is the fat contained in cow's milk.[1]

Normal cow butter, not salted, has, according to *Koenig*, the following composition:—

Fat	87·0 per cent
Casein	0·5 ,,
Milk Sugar	0·3 ,,
Ash	0·3 ,,
Water	11·7 ,,

The percentage composition of butter varies, however, to a considerable extent (see below), the proportion of fat, on the one hand, rising in some cases to 95 per cent, whereas, on the other hand, the amount of water may reach as high a figure as 35 per cent if the churning be carried out at a high temperature.

Good English butter has, according to *Bell*, the following composition:—

Fat	90·27 per cent
Curd	1·15 ,,
Salt	1·03 ,,
Water	7·55 ,,

Vieth has derived from a large number of analyses of butters the following figures:—

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[1] The following characteristics of the milk fats from other animals have been published:—

Milk Fat from	Specific Gravity. At 15° C.	Specific Gravity. At 100° C.	Solidifying Point.	Melting Point.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Hehner Value.	Refractive Index.	Unsaponifiable Matter. — Per cent.	Observer.
Goat .	0·9312	0·8669	24·31	27-38·5	221·6	30·4-34·6	23·1-25·4	86·5-87·3	1·4596	..	Solberg
,, .	..	..	31	36·5	..	..	28·6	..	..	..	Pizzi
Sheep	..	..	..	29-30	..	..	32·9	..	..	..	,,
Mare .	..	..	..	..	..	..	11·2	..	..	..	,,
Ass .	..	..	..	..	..	..	13·1	..	..	..	,,
Buffalo	..	..	29	38	..	..	26·2	..	..	..	,,
,, (Bulgarian)	..	0·8692	..	..	220·0	36·75	34·2	88·19	..	..	Petkow *
Reindeer .	0·9428	0·8640	34-39	37-42	219·2	25·1	31·4	86·89	1·4647	..	Solberg
Gamoose (Buffalo)	..	..	..	..	220·4-231·7	32-35	34·7-35	86·9-87·5	..	..	H. D. Richmond
Woman .	..	0·870	..	..	218·4	43·4	15·8 †	89·2	..	4·68 ‡	Sauvaitre ‖

* *Zeit. Nahrungs. u. Genussm.* 1901, 826.

† Total volatile acids 4·41 per cent. Ratio of butyric acid to caproic acid 2·4 : 1.

‡ A normal cow butter gave 1·58 per cent. of unsaponifiable matter.

‖ *Annal. Chim. analyt.* 1902, 143. Cp. also A. Jolles, *Chem. Zeit.* 1903, 505.

Origin of Butter.	Fat.	Curd.	Salt.	Water.
	Per cent.	Per cent.	Per cent.	Per cent.
English . .	86·85	0·59	1·02	11·54
French . .	84·77	1·38	0·09	13·76
„ salted .	84·34	1·60	2·01	12·05
Kiel . . .	85·24	1·17	1·35	12·24
Danish . .	83·41	1·30	1·87	13·42
Swedish . .	83·89	1·33	2·03	13·75

The examination of butter divides itself naturally into two parts: (1) The examination of the whole butter; (2) The examination of the butter fat.

Under the first heading I shall consider the examination of butter on the assumption that the butter fat contained in it is genuine.

1. Examination of Butter

The examination of butter comprises the determination of the **water**, **solids-not-fat**, **colouring matters**, and **preservatives**. Gross adulterants, such as *starch*, *potato pulp*, *ground white cheese*, etc., will hardly occur nowadays, since the adulteration of butter has assumed a more scientific character, and is practically confined to the adulteration of the butter fat with foreign fats. This will be considered under Examination of Butter fat.

1. **Water** is determined by drying the sample at 100° C. The Society of Bavarian Analytical Chemists recommend drying the butter at 100° C. for six hours, with occasional stirring.[1]

In cases where scientific accuracy is not the chief object, as for market control, the amount of water may be determined rapidly by *Birnbaum's* method as modified by *Wibel*[2] in the following manner: 10 grms. of butter are shaken up with 30 c.c. of ether, saturated with water, in a tube corked at one end and provided with a stopcock at the other, through which the separated aqueous liquid is run off into a second narrow graduated tube, containing 5 c.c. of saturated brine and a trace of acetic acid, so as to give a distinct red colour with litmus. The increase of volume, due to the water in the butter, is then read off. The results are stated to be but slightly below those obtained by gravimetric analysis.[3]

The proportion of water in butter should not exceed 16 per cent. *J. Bell* found in the analysis of 113 genuine English butters values varying from the minimum of 4·15 to the maximum of 20·75 per cent; the majority of samples, however, contained from 11-14 per cent. The following table gives a few values culled from analyses

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[1] For Crismer's method of determining the amount of water by means of the critical temperature of dissolution the reader must be referred to the *Bullet. de l'Assoc. Belge des Chim.* 1896 (9), 359; *Analyst*, 1896, 241.

[2] *Journ. Soc. Chem. Ind.* 1893, 630.

[3] Cp. also *Poda*, *Zeit. f. Unters. Nahrungs. u. Genussm*, 1901, 492. G. R. Geldard, Eng. Pat. 18,496, 1902; M. Vogtherr, French Pat. 324,745, 1902.

by *Vieth* and *H. D. Richmond*,[1] and arranged by the writer according to their percentages of water:—

Kind of Butter.	Number of Samples examined.	Samples containing per cent of Water.			Observer.
		From 11-14.	From 10-15.	Above 16.	
		Per cent.	Per cent.	Per cent.	
English and foreign . .	560	83·8	94·2	0·9	Vieth
English . . .	143	70·7	85·4	0·7	H. D. Richmond
Foreign . . .	417	88·3	97·2	1·0	,,
French . . .	451	...	...	8·6	,,
,, . . .	48	...	...	0·0	,,

In the following table *Martiny's*[2] numbers, referring to more than 20,000 separate tests, are collated:—

Country.	Water. Per Cent.	Number of Samples.
England . .	11·18	334
Germany—		
Fresh butter .	13·96	523
Salt butter .	13·01	1107
France . .	13·40	225
Denmark . .	13·99	9847
Sweden . .	13·66	4423
Finland . .	11·18	438

If butter is made at a somewhat high temperature—as is the case in the West of Ireland—the water cannot be removed so readily as in dairies in which the cream is cooled properly; the proportion of water in "Irish butter" is therefore higher, rising to 25 per cent and more.

In this country the limit of 16 per cent for the proportion of water in butter has been legalised, and such exceptional butter as Irish butter can only be sold provided a sufficient disclosure is made to the purchaser.

There is, however, in commerce **milk-blended butter**, an artificially prepared butter, containing from 20-25 per cent of water. It is manufactured by incorporating milk with butter, and adding preservatives so as to prevent the milk from "souring." It is evident that this is tantamount to incorporating water with butter. At first this adulterated butter was sold as "butter," but owing to the interference of the law the name was changed into "milk-blended butter."[3]

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[1] *Analyst*, 1894, 17.

[2] *Landw. Jahrb.* 1898, 773.

[3] Although this mixture of milk and butter has been the subject of numerous prosecutions under the Sale of Food and Drugs Acts, there has no High Court decision been given as yet in this matter, so that it is meanwhile held that the seller of milk-blended butter is protected provided that a sufficient disclosure be made to the purchaser at the time of sale.

2. **Solids-not-fat** are best determined in the sample of butter previously employed for the estimation of water, by exhausting the dried butter with ether, chloroform, carbon bisulphide, or petroleum ether, and weighing the residue after drying.

If a fresh quantity of butter be taken for this determination, due attention must be paid to the fact that butter is not a homogenous product, different parts of the sample containing varying amounts of butter milk.

The solids-not-fat consist of *casein*, *milk-sugar*, and *inorganic salts.* By exhausting the dried residue with water, to which a trace of acetic acid has been added, milk-sugar and the bulk of the inorganic salts are removed, leaving casein behind; its weight is ascertained after drying. The minute quantity of salts retained in the casein and found on incineration is deducted. *Koenig* suggested to determine the proportion of nitrogen by *Kjeldahl's* process and multiply it by 6·25. Both methods yield identical results. The percentages of casein (curd) recorded by *Koenig* for 302 samples of butter vary from 0·19 to 4·78 per cent.

The amount of *inorganic salts*, chiefly sodium chloride, is found by igniting the ether-insoluble residue from 10 grms. of butter, taking care, however, not to heat the ash to too high a temperature lest sodium chloride should volatilise. The proportion of sodium chloride is determined by titration with standard silver solution, using potassium chromate as an indicator. Sodium chloride is determined with greater accuracy by melting in a porcelain dish 10 grms. of butter with an equal amount of paraffin wax and 50 c.c. of water, acidulated with a few drops of nitric acid, and stirring the melted mass. After cooling, the cake is taken off, rinsed well, the aqueous liquid filtered, and precipitated with silver nitrate.

The proportion of sodium chloride in the 113 samples examined by *J. Bell* was found lying between 0·4 and 9·20, the majority of the samples yielding from 2 to 7 per cent; in only one case 15·08 per cent was found. The amount of salt added to butter varies, of course, in different countries and localities. An excessive amount of ash will naturally invite further examination.

Milk-sugar is not determined direct, but found by difference.

The proportion of *butter fat* is likewise found by difference; it can, of course, be determined direct by evaporating the ether-extract and weighing the residue.

Fraudulently added substances of a non-fatty nature, such as *starch*, *borax*,[1] etc., are detected as described page 147.

3. **Colouring Matters.**—Summer butter is yellow, winter butter is almost white;[2] the latter is therefore, as a rule, coloured artificially before being placed on the market. The naturally yellow butter is rapidly bleached when exposed to light and air.

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[1] In Italy the admixture of 2 grms. of borax per 1000 grms. of butter is permitted.

[2] In this connection it may be interesting to note that in some Swiss farms having an abundant growth of *Leontodon* and *Ranunculus*, the cows gave butter of such intense yellow colour that suspicion was aroused; the butter obtained after the second grazing was very much paler.

Foreign colouring matters, "butter colouring," are detected by shaking the melted butter with alcohol. In presence of foreign colouring matters the alcoholic layer becomes tinted, whereas natural butter leaves the alcohol colourless.

Moore[1] and *Martin*[2] recommend the use of a mixture of alcohol and carbon bisulphide. According to *Martin*, 5 grms. of butter are shaken up with 25 c.c. of a mixture consisting of 15 parts of methyl alcohol, or ordinary alcohol, and 2 parts of carbon bisulphide. Two layers are formed, the lower one consisting of the fat dissolved in carbon bisulphide, the upper alcoholic layer containing the colouring matter.

Stebbins,[3] however, has pointed out that the small quantity of fat retained by the alcoholic layer may interfere with the subsequent examination, and that carotin, the colouring matter from carrot juice, is more easily soluble in carbon bisulphide than in alcohol. He substitutes, therefore, the following process:—Melt 50 grms. of the sample in a beaker on the water-bath, stir into the melted mass 5 to 10 grms. of finely powdered fuller's earth, agitate thoroughly for two or three minutes, and allow to settle out completely whilst warm. Drain off the bulk of the fat, add 20 c.c. of benzene, stir well, allow to deposit, and decant the solution through a filter. Repeat this process until the fat is completely removed, and wash the precipitate on the filter with benzene. Test the filtrates for carotin. Dry the precipitate on the water-bath, and boil out three times with about 20 c.c. of 94 per cent alcohol. Evaporate the alcoholic extracts in a tared dish, dry at 100° C., and weigh the residue. The residue obtained by the one or the other method is then examined by means of special reactions for the colouring matter present.

Turmeric (*curcuma*) and **annatto** are at present chiefly used in France. A preparation for colouring butter is sold there under the name of "jaune gras" (fat yellow), made by digesting annatto with sesamé oil and then adding to it turmeric.

Turmeric is indicated by the appearance of a brownish-yellow colouration on adding a few drops of ammonia, and of a reddish-brown colouration on subsequently adding hydrochloric acid.

Annatto is identified by a reddish-brown residue, dissolving in concentrated sulphuric acid with production of a blue colour.

In the presence of *saffron* an orange coloured precipitate is obtained on dropping lead acetate into the aqueous solution of the residue.

Leeds[4] dissolves 100 grms. of butter in 300 c.c. of pure petroleum ether, of 0·638 specific gravity, in a separating funnel, draws off the curd and water, and washes several times with water, using about 100 c.c. The solution of butter fat is then kept at 0° C. for about twelve to fifteen hours, so that the bulk of the solid glycerides may crystallise out. The liquid fat is poured off and shaken with

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[1] *Analyst*, 11, 163.

[2] *Ibid.* 12, 70.

[3] *Journ. Amer. Chem. Soc.* 1887, 41.

[4] *Analyst*, 1887, 150.

50 c.c. of decinormal alkali, to remove the colouring matters from the ethereal solution. The aqueous layer is drawn off and carefully titrated with hydrochloric acid, until just acid to litmus. The colouring matters, containing a minute quantity of fatty acids, are thus precipitated; the precipitate is transferred to a tared filter, washed with cold water, dried, and weighed.

For the discrimination of the several colouring matters the precipitate is dissolved in alcohol and two or three drops of the solution tested with an equal quantity of the reagents given in the following table:—

Reactions of Colouring Matters

Colouring Matters.	Concentrated H_2SO_4	Concentrated HNO_3	$H_2SO_4+HNO_3$	Concentrated HCl.
Annatto	Indigo blue, changing to violet	Blue, becoming colourless on standing	Same	No change, or only slight dirty yellow and brown
Annatto+ decolourised butter	Blue, becoming green, and slowly changing to violet	Blue, then green and bleached	Decolourised	No change, or only slight dirty yellow
Turmeric[1]	Pure violet	Violet	Violet	Violet, changing to original colour on evaporation of HCl
Turmeric+ decolourised butter	Violet to purple	Violet to reddish violet	Same	Very fine violet
Saffron.	Violet to cobalt blue, changing to reddish brown	Light blue, changing to light reddish brown	Same	Yellow, changing to dirty yellow
Saffron+ decolourised butter.	Dark blue, changing quickly to reddish brown	Blue, through green to brown	Blue, quickly changing to purple	Yellow, becoming dirty yellow
Carrot.	Umber brown	Decolourised	Do. with NO_2 fumes and odour of burnt sugar	No change
Carrot+ decolourised butter	Reddish brown to purple, similar to turmeric	Yellow, and decolourised	Same	Slightly brown
Marigold	Dark olive green, permanent	Blue, changing instantly to dirty yellow green	Green	Green to yellowish green
Safflower	Light brown	Partially decolourised	Decolourised	No change
Aniline yellow	Yellow	Yellow	Yellow	Yellow
Martius yellow	Pale yellow	Yellow, reddish precipitate. Magenta at margin	Yellow	Yellow, precipitate treated with NH_3 and ignited; deflagrates
Victoria yellow	Partially decolourised	Same	Same	Same, colour returns on neutralising with NH_3

According to *Leffmann*,[2] methylorange is extensively used in the U.S.A., especially for "oleomargarine." The colouring matter is ex-

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[1] Ammonia gave with turmeric a reddish-brown colour which reverted to the original colour on driving off the ammonia

[2] Second annual report of the Dairy and Food Commissioner of Pennsylvania.

tracted as described above and tested with dilute acid, when the well-known red tint will appear.

Geisler[1] states that annatto is now largely replaced in the United States by a yellow azo dye, and used in combination with an orange dye (methylorange?). The dye can be extracted from the fat by agitating with fuller's earth from which the colouring matter in its turn can be extracted by boiling alcohol. The isolated dye dissolves in concentrated sulphuric acid giving a yellow coloration which changes to red on the addition of water. (Methylorange does not behave in the same manner with fuller's earth.)

Grünhut[2] proposes to detect colouring matter by dyeing wool with an extract of colouring matter. He therefore saponifies the sample in the cold (p. 58), evaporates the petroleum ether and the bulk of the alcohol, dissolves in water and acidulates slightly, so that the fatty acids just commence to separate, renders slightly alkaline with sodium carbonate, and heats to boiling after adding some wool. Dimethylamidoazobenzene cannot be detected by dyeing tests. Its presence must be proved spectroscopically, after the colouring matter has been extracted from the soap solution by means of petroleum ether. Annatto is detected by dyeing wool fibre.

Butter colours are similarly treated, using, of course, smaller quantities of the samples. About 5 grms. are dissolved in 20-25 c.c. petroleum ether, and treated with 10 c.c. of a 4 per cent solution of potash.[3]

4. **Preservatives.**—*Borax* will be discovered on examining the ether-insoluble portion.

Boric acid is detected by adding some caustic potash to 10 grms. of butter fat and incinerating in a platinum dish. The ash is acidified with hydrochloric acid, and tested with turmeric paper.

Since the Preservatives Committee recommend a limit of 0·5 per cent of boric acid in butter, the determination of boric acid may be required. *Richmond* and *Harrison*[4] (using a slight modification of *Thomson's* method) recommend the following process:—About 25 grams of butter are weighed into a stoppered cylinder, enough water to make with the water already present 25 c.c. and 10 to 15 c.c. of chloroform are added; the contents of the cylinder are warmed, mixed, and allowed to separate; an aliquot portion of the aqueous solution is drawn off (each c.c. containing the boric acid of 1 gram of butter), made alkaline, evaporated, ignited, and the ash extracted with hot water. The solution is made neutral to methylorange, boiled to expel carbon dioxide, and titrated with standard alkali

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[1] *Journ. Amer. Chem. Soc.* 1898, 110.

[2] *Chem. Centr. Blatt.* 1898, ii. 943.

[3] The following formulæ for butter colours have been taken by *Leffmann* from a *Druggist's Circular*:—

Extract of Annatto	10	ounces.
Turmeric . .	5	,,
Logwood chips .	2½	,,
Cotton seed oil .	1	gallon.

Annatto seed, bruised	10	parts.
Turmeric . . .	3	,,
Ammonium carbonate	1	,,
Cotton seed oil . .	75	,,
Lard	10	,,

[4] *Analyst*, 1902, 179.

after the addition of glycerol. That part of the ash which is insoluble is free from boric acid. For further details and improvements of the process suggested by *Warren*, the original paper must be consulted.[1]

A more accurate gravimetric method for the determination of boric acid is given by *Partheil* and *Rose*.[2]

Salicylic acid is sometimes used to preserve butter.[3] It is detected by shaking the butter with twice its volume of 20 per cent alcohol and a few drops of dilute ferric chloride. In the presence of salicylic acid the aqueous layer shows a violet tint.

Formalin (formaldehyde) is best detected by *Hehner's* method in the form given to it by *Richmond* and *Boseley*:[4] Add to the aqueous liquor obtained when butter is melted, a drop of milk, and pour the mixture carefully on the surface of concentrated sulphuric acid contained in a test-tube. In the presence of formalin a blue ring will appear at the zone of contact of the two liquids. A trace of ferric chloride renders the reaction far more distinct. The German official method directs to place 50 grms. of butter in a 250 c.c. flask together with 50 c.c. of water, to warm the mixture on the water bath, and to distil off 25 c.c. in a current of steam. To 10 c.c. of the distillate 2 drops of an ammoniacal solution of silver nitrate are added, and the mixture allowed to stand in the dark. From the reduction of silver nitrate the presence of formalin is inferred. This method is, however, not free from objection, since butter made from ripened cream may contain volatile silver-reducing substances.[5]

Glucose.—In the United States glucose is used as a preservative for export butter.[6] It is detected by washing the butter repeatedly with hot water and testing the aqueous solution with Fehling's solution. The fact should, however, not be overlooked that a *slight* reduction may be due to milk sugar or some of the albuminoids.

Fluorides have recently been used as butter preservatives, especially for butter from Brittany.[7] A butter preservative is sold there consisting of about 98 per cent of sodium fluoride.

The presence of fluorides is detected by melting about 50 grms. of butter, separating the aqueous layer, rendering it alkaline, and evaporating the latter to dryness. The ignited residue is then treated in a platinum crucible with strong sulphuric acid, the crucible being covered with a wax-coated watch-glass, into which a mark has been scratched. The crucible is heated on a sand bath for two hours. In the presence of even one milligram of calcium-, or sodium fluoride, the glass will be found distinctly etched.

Since in the presence of a boric preservative boron fluoride is evolved by strong sulphuric acid, the formation of boron fluoride must be avoided by the use of dilute sulphuric acid, and as long as the amount of boric acid does not exceed five times the amount of

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[1] *Analyst*, 1902, 182.

[2] *Berichte*, 1901, 3611.

[3] *Journ. Soc. Chem. Ind.* 1887, 670.

[4] *Analyst*, 1895, 155; 1896, 92, 94, 157.

[5] Cp. Mayrhofer, *Zeit. Unter. Nahrgs. und Genuss.*, 1898, 552.

[6] Crampton, *Journ. Amer. Chem. Soc.* 1898, 201. *Analyst*, 1898, 130.

[7] O. and C. W. Hehner, *Analyst*, 1902, 173.

the fluoride present, the etching of the glass can be obtained. It is, however, preferable to remove the boron compounds at first. This is done by separating the aqueous liquor from 50 grms. of butter, adding calcium chloride, and heating to boiling after a small excess of sodium carbonate has been added. The precipitate (consisting of calcium borate, calcium fluoride, calcium carbonate, calcium phosphate, and perhaps traces of sulphate), is filtered off, ignited, and the residue treated with hot dilute acetic acid to remove the carbonate, borate, and phosphate. The residue is then filtered off, ignited, and treated with strong sulphuric acid as described above.

The presence of fluorides, as also of formalin, must be considered as harmful. In order to preserve butter in a harmless manner salt is added to it.

"**Renovated**" butter or "**process**" butter is manufactured in large quantities in the United States. It is stated that during 1902 the production of "process" butter amounted to 5,879,833 lbs., about half the quantity of margarine ("oleomargarine") made in the United States. It is manufactured from unsaleable, "rancid" butter, by melting and separating the butter fat from the aqueous solution and the curd. The butter fat is then blown with air to remove the objectionable flavour, and then quickly cooled in a current of cold water, so as to prevent the separation of the more liquid portion of the butter ("butter oil") from the more solid portion. The butter fat is then churned with fresh milk to which cultures of suitable bacteria have been added. The milk soon becomes sour and coagulates, thus furnishing an artificial curd, containing about the same proportions of nitrogen as the curd of genuine butter. It is evident that by chemical methods alone "renovated butter" cannot be distinguished from genuine butter, the fat contained in such butter being, of course, genuine butter fat, and the proportions of the constituents being, as a rule so regulated as to simulate the composition of a normal butter. This is exemplified by the mean of seventy-five analyses of process butters published by *Crampton*:[1]—

	Maximum.	Minimum.	Mean Value.
	Per cent.	Per cent.	Per cent.
Fat . . .	88·88	68·80	82·05
Curd . .	2·65	0·77	1·47
Ash . . .	7·49	0·97	2·85
Water . .	23·17	8·01	14·44

Hess and *Doolittle*[2] propose to detect renovated butter by the appearance of the curd, as the curd from process butter is the milk-caseïn, whereas the curd from normal butter is the proteïd of cream. Certain differences, such as the different appearance under a polarisation microscope, will be noticeable. For the details the reader must

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[1] *Journ. Amer. Chem. Soc.* 1903, 358.

[2] *Ibid.* 1900, 150.

be referred to the original paper, and it need only be added that, according to *Hess* and *Doolittle*, "butter process," does not yield a clear layer of fat on melting, even after some prolonged standing, whereas in the case of pure butter the fat becomes clear soon after melting.

In commerce, butter is not merely valued by its purity (as ascertained by the tests described in the foregoing lines, and the chemical tests for butter fat to be described below), but its value depends also to a considerable extent on its flavour and taste. A proper valuation of butter on the strength of the last two named tests hardly belongs to the province of the analytical chemist, as it requires a good deal of practice, which is not based on chemical evidence. It may, however, be pointed out that the peculiar aroma of a good butter is due to the action of a bacterium which gives rise to the formation of the flavouring substance during the ripening of the cream. That this is the case is shown by the general experience that the desired butter aroma does not appear in sweet cream butter, such butter having what is termed a "flat" insipid taste. A bacterium of this kind was first isolated by *Storch*. *Weigmann* described two forms or races, one of which develops an exquisite flavour and aroma, but causes the butter to keep badly, whilst the second race develops less aroma whereas the butter keeps better. The cultivation of cream-ripening bacteria has been considerably advanced in America by *H. W. Conn*.[1] Laboratory experiments having demonstrated that a particular butter bacillus can produce a pleasant flavour, if inoculated into the cream in the process of ripening under such conditions that it can grow rapidly, pure cultures of this bacillus were distributed amongst the numerous dairies. By this means the "June flavour," which had hitherto only been met with in butter of certain districts during a short season of the year, can now be produced by artificial means. This flavour is stated to be retained in the butter even for a longer period than the flavour which is obtained without such aid in ripening. In addition to the fine flavour a somewhat enhanced keeping property is said to be imparted to the butter.

The presence of curd and water in butter renders it far more liable to become rancid than is the case with pure butter fat. Hence in some countries, as for instance in South-West Germany, butter is melted until the butter fat has become quite clear, whereupon the latter is separated from the curd and water. The flavour of such butter ("Schmelzbutter") suffers, however, considerably. The literature dealing with the rancidity of butter is a very voluminous one, but unfortunately a number of writers seem to have confounded butter fat with butter. The conditions influencing the liability of

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[1] Cp. *Bacteria in Milk and its Products*. London, 1903. Rebman, Limited.

butter fat to rancidity have been fully explained in Chapter I. (pages 19 to 28); and although it has been pointed out above that rancidity is not coterminous with acidity, it is still the practice of some analysts to determine the amount of free fatty acids in butter fat in order to arrive at a measure of rancidity (cp. below).

The conditions favouring the rancidity of butter fall outside the scope of this work, and the reader must therefore be referred to the original papers given in the footnote.[1]

On exposure to light, butter loses its yellow colour, and acquires a tallowy ("lardy") smell and taste.

II. Examination of the Butter Fat

For tables of constants see pp. 834-836.

Pure butter fat consists almost exclusively of triglycerides of fatty acids. Besides triglycerides, butter fat contains cholesterol and some natural colouring matters (lactochromes). The total amount of unsaponifiable matter is less than a half per cent (0·35 per cent *Bömer*; 0·42 per cent *Klein* and *Kirsten*[2]). Lecithin has been stated by various observers to occur in butter fat to the extent of 0·017 or even 0·15 to 0·17 per cent (calculated from phosphoric acid). *Jaeckle*, however, showed that butter fat contains no compound of phosphorus.

The following acids have been identified hitherto in butter fat:—acetic, butyric, caproic, caprylic, capric, lauric, myristic, palmitic, stearic, arachidic, and oleic. *Wachtel*, and also *Bondzyński* and *Rufi* stated that butter fat contains hydroxylated acids, and on the strength of these statements, obtained by the application of faulty methods, *Browne*[3] has even calculated the percentage of hydroxylated acids. Experiments made by the writer prove, however, that butter contains practically no hydroxylated acids, the low acetyl values obtained being due to the presence of small quantities of mono- and diglycerides.

The extraordinarily high percentage of glycerides of soluble fatty acids in butter fat is characteristic.

The quantity of stearic acid found by the method described p. 354 seems to be very small. In an analysis carried out in my laboratory with a sample of butter fat of the *Reichert-Meissl* value

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[1] Schmidt, *Zeit. f. Hygiene u. Infectionskrankheiten*, 1898, 163; Hanus, *Zeit. f. Unters. Nahrgs. u. Genussm.* 1900, 324; Hanus and Stocky, *ibid.* 606; Lydia Rabinowitsch, *Jahrbuch d. Chemie*, ix. 237; Crampton, *Journ. Amer. Chem. Soc.* 1902, 711; Orla Jensen, *Jahrbuch d. Chemie*, xii. 363; O. Laxa, *Arch. f. Hygiene*, 1902, 119.

[2] *Zeit. f. Unters. Nahrg. u. Genussm.* 1903, 147.

[3] *Journ. Amer. Chem. Soc.* 1899, 613

28·1, the amount of stearic acid found in the insoluble fatty acids was only 0·49 per cent (see p. 406). The presence in a normal butter of less saturated acids than oleic acid has not yet been proved beyond doubt. *Farnsteiner* has shown that in the butter from a cow fed on cotton meal, traces of linolenic acids were ascertainable. *Partheil* and *Ferié* (see below), state that less saturated acids than oleic occur in butter fat to a somewhat considerable extent; but as the method by which their presence was determined is not free from objection (p. 367), this statement must be accepted with reserve.

The approximate composition of the several fatty acids in a sample of butter fat examined by *Bell* is stated as follows:—

Butyric acid	6·13	per cent
Caproic, caprylic, and capric acids	2·09	,,
Palmitic, stearic, and myristic acids	49·46	,,
Oleic acid	36·10	,,
Glycerol	12·54	,,
	106·32	

The fatty acid which was soluble in water at 15·5° C. was considered to be butyric acid. The second group—caproic, caprylic, and capric acids—comprises the acids soluble in hot water; their mean molecular weight was calculated to 136 from the analysis of their mixed barium salts. The product obtained on decomposing the ether-soluble lead salts of the insoluble fatty acids was judged to be oleic acid; the mixed palmitic, stearic, and myristic acids were calculated by difference.

According to *Duclaux*,[1] butter fat contains from 2 to 2·26 per cent of caproic, and from 3·38 to 3·65 per cent of butyric acid. From the analyses of twenty-eight butter fats, *Violette*,[2] somewhat arbitrarily, assumes the proportion in which butyric acid stands to caproic in butter fat to be 1·645. Thus he is enabled to calculate severally the proportions of butyric, caproic, solid volatile, and insoluble fatty acids by proceeding in the following way:—50 grms. of butter fat are saponified and the volatile acids separated, as in *Reichert's* distillation process. The solid volatile acids are separated by filtration, and their quantity determined after drying; the amount of the fixed (insoluble) fatty acids is arrived at in the same way. The total quantity of the soluble acids is ascertained by titration with decinormal alkali, and calculated to butyric acid. If A represent this quantity of butyric acid, then the quantities of butyric and caproic acids B and C can be calculated with the help of the following equations:—

$$B = A \times 0{\cdot}68469$$
$$C = A \times 0{\cdot}41565.$$

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[1] *Compt. rend.* 102, 1022.

[2] *Journ. Soc. Chem. Ind.* 1890, 1157.

Physical and Chemical Constants of Butter Fat

Specific Gravity.			Solidifying Point.		Melting Point.[1]		Saponification Value.		Iodine Value.	
C		Observer.	C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
15	0·936-0·940	Hager	19-20	Wimmel	31-31·5	Hehner	227	Köttstorfer,	26·0-35·1	Hübl
,,	0·9275	Winter Blyth	..	..	29·5-34·7	Bell	(221·5-233·4)	Valenta, Moore, Allen, etc.	25·7-37·9[4]	Wollny
,,	0·926	Casamajor	..	..	29·4-33·3	Cameron			28-32	Thoerner
37·8 (100 F.)	0·911-0·913	Bell	20-23	Thoerner	28-33	Thoerner	225-230	Thoerner		
40 (water at 15·5=1)	0·9041	Allen					221-233	Seyda and Woy[2]		
100 (water at 15=1)	0·865-0·868	Koenigs					219·7-232·6	Thorpe[3]		
100 (water at 15·5=1)	0·867-0·870	Allen								
100 (water at 100=1)	0·901-0·904	Wolkenhaar								
,,	0·9094-0·9140	Bell								
,,	0·9105-0·9138	Muter								
,,	0·9099-0·9132	Allen								

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[1] According to Meyer (*Milch-Zeit.* 1892, 49), the melting point of cow butter is lowered by food consisting of easily digestible carbohydrates, but raised by straw, oil cakes, or sour fodder.

[2] Silesian butters.

[3] Calculated by me from the "saponification equivalents" of 357 English butters.

[4] 56 samples, mean 33·32.

Physical and Chemical Constants of Butter Fat—continued

Reichert Value.		Hehner Value.		Thermal Test. Heat of Bromination.		Refractive Index.		
c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	° C.	Observer.	At 0 ° C.		Observer.
14 (12·5-15·2)	Reichert, Moore, Allen, etc.	87·5 86·45-89·8	Hehner Bell	6·6-7·0 9·5	Helmer and Mitchell Broomwell and J. L. Meyer	25 60	1·4590-1·4620 1·445-1·448	Wollny. Thoerner

Reichert-Meissl Value.	
20·63-33·15	Cp. p. 846.

Oleo-refractometer.	
"Degrees." At 45° C.	Observer.
−29 to −31	Jean
−25 to −31	Pearmain

Butyro-refractometer.		
At ° C.	Scale Divisions.	Observer.
25	52·5	Skalweit
25	49·5-54	Wollny
35	44·8-47	Besana
40	41-42	Mansfeld
40	40·5	Beckurts and Seiler
40	40·5-44	Delaite
45	39·4-42	Thorpe

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.		Solidifying Point.		Melting Point.[1]		Neutralisation Value.[2]	
At 37·75° C. (water 15·5° C.=1).	Observer.	° C.	Observer.	° C.	Observer.	Mgrms. KOH.	Observer.
0·9075-0·9085	Leonard	35·8	Hübl	38	Hübl	210-220	Thoerner
0·90919-0·91357	Bell	37·5-38	Paris Municipal Laboratory	41-43 and 43-45	Bensemann		
		33-35	Thoerner	38-40	Thoerner		

Physical and Chemical Constants of the Mixed Fatty Acids—continued

Iodine Value.		Heat of Bromination.		Refractive Index.	
Per cent.	Observer.	° C.	Observer.	At 60° C.	Observer.
28-31	Thoerner	6·2	Hehner and Mitchell	1·437-1·439	Thoerner

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[1] Butter from cows fed on cotton seed cakes have a considerably (by 8° to 9° C.) higher melting point (Lupton, *Journ. Amer. Chem. Soc.* 1891, 134).

[2] The neutralisation value of the fatty acids obtained after distilling off the volatile fatty acids by Reichert's process were found 213·3 to 218·9 (Henriques).

In the following table *Violette's* results are reproduced :—

Fatty Acids.	Superior Qualities of Butter.			Inferior Qualities of Butter.				
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Butyric acid . .	6·07	5·33	5·50	5·05	4·62	4·80	4·76	4·37
Caproic acid . .	3·66	3·23	3·34	3·06	2·80	2·92	2·89	2·65
Solid volatile acids	2·85	3·00	2·80	3·00	2·90	2·40	3·00	2·95
Non-volatile acids . .	82·28	82·63	82·87	83·20	84·32	84·31	83·83	84·62
Total . .	94·76	94·19	94·41	94·31	94·64	94·43	94·48	94·59

By ascertaining finally the mean molecular weights of the solid volatile and of the non-volatile acids, *Violette* obtained all the data necessary for calculating the percentage composition of the butter fats. This is given in the following table :—

Glycerides.	Superior Qualities of Butter.			Inferior Qualities of Butter.				
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Butyrin	6·94	6·09	6·28	5·76	5·28	5·49	5·45	5·00
Caproin	4·06	3·58	3·70	3·39	3·09	3·23	3·10	2·94
Glycerides of solid volatile acids . . .	3·06	3·22	2·96	3·16	3·06	2·53	3·16	3·15
Glycerides of non-volatile acids . . .	85·98	86·62	86·60	86·93	88·10	88·10	87·60	88·42
Difference . . .	0·04	0·49	0·46	0·76	0·47	0·65	0·69	0·49
	100	100	100	100	100	100	100	100

I subjoin a table showing the composition of butter fat, calculated by me from *Bell's* results, and as given by other observers :—

Glycerides.	J. Bell.	W. Blyth.	Spallanzani.[1]
	Per cent.	Per cent.	Per cent.
Butyrin . . .	7·012	7·7	5·080
Caproin . . .	2·280	0·1	1·020
Caprylin and caprin .			0·307
Olein	37·730	42·2	93·593
Palmitin, stearin, etc. .	52·978	50·0	
	100	100	100

I have shown above (chap. xi. p. 405) how the theoretical composition of a butter fat may be calculated from the numbers obtained on examining butter fat by the quantitative tests. In the

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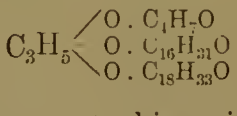
[1] *Le Staz. Sperim. Ital.* vol. iv. 417.

example given there the volatile fatty acids were found by difference; the volatile acids may be further resolved into soluble volatile and insoluble volatile acids (*Violette's* solid volatile acids; cp. also *Polenske's* method, p. 853). The calculated mean molecular weight of the soluble volatile acids was 112.[1] In the example, p. 405, stearic acid was determined direct; the sum of all other saturated fatty acids was obtained by difference. The lithium salt method of *Partheil* and *Ferié* (p. 353) would admit of a further resolution of the *insoluble* acids into their several components. *Partheil* and *Ferié* arrived at the following composition of the insoluble fatty acids of a sample of butter fat having the iodine value 35·2, and the Reichert-Meissl value 33·1 :—

Stearic acid	6·65	per cent.
Palmitic acid	18·23	,,
Myristic acid	11·08	,,
Lauric acid	16·39	,,
Unsaturated acids, of which 5·4 per cent were less saturated than oleic acid . .	30·67	,,
	83·02	,,

The extraordinarily high amount of stearic acid is at variance with the numbers found by *Hehner* and *Mitchell* and by myself. Furthermore, on calculating from the above given composition the mean molecular weight of the fatty acids, and allowing for the unsaturated fatty acids the mean molecular weight 280, I arrive at the mean molecular weight of 252, which is lower than the mean molecular weights of the insoluble fatty acids obtained hitherto.[2] Hence the composition given by *Partheil* and *Ferié*, although derived from two analyses, must be accepted with reserve.

It appears very likely that at least some of the triglycerides contained in butter fat are "mixed glycerides." The opinion that mixed glycerides occur in butter fat was first pronounced (before oleo-distearin was isolated, page 16) by *J. Bell*,[3] on the strength of experiments made by *G. Lewin*, of the Government Laboratory. *Bell* stated that a mixed glyceride of the following composition occurs in butter fat:—



$$C_3H_5\begin{cases} O\,.\,C_4H_7O \\ O\,.\,C_{16}H_{31}O \\ O\,.\,C_{18}H_{33}O \end{cases}$$

The following facts support this opinion: If ordinary animal fat is melted and mixed with—say 10 per cent of—butyrin, the

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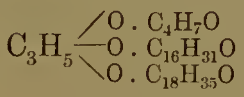
[1] Recently Juckenack and Pasternack (*Zeit. f. Unters. Nahrungs. u. Genussm.* 1904, 204) gave the mean molecular weights of the soluble volatile acids of butter fats having the Reichert-Meissl values 26·3-27·5 as 95·1 to 98·3.

[2] Thorpe (*Journ. Chem. Soc.* 1904, 254) found the mean molecular weights of the insoluble fatty acids of ten butter fats (of the Reichert-Wollny numbers 32·6, 257·8 (cp. table given below). Juckenack and Pasternack quite recently found (*Zeit. f. Unters. Nahrungs. u. Genussm.* 1904, 204) the mean molecular weights of the insoluble fatty acids of butter fats (of the Reichert-Meissl numbers 26·3-27·5) 260·2-260·6.

[3] *The Chemistry of Foods*, ii. 44.

latter may be entirely removed by digestion with alcohol, the animal fat being recovered practically in its original condition. If, on the contrary, butter fat is treated with hot alcohol, from 2 to 3 per cent only of its weight passes into the alcohol. The fat thus dissolved does not consist of butyrin or caproin, but of a fat which is liquid at 15·5° C., and yields, on saponification, from 13 to 14 per cent of soluble fatty acids, and from 79 to 80 per cent of insoluble fatty acids. The latter have a higher melting point than the mixed insoluble acids obtained from the original butter fat; this tends to disprove the opinion that the low melting point of the extracted fat might be due to an increased proportion of oleic acid in its molecule. These results agree closely with a compound of the above given formula, which *Bell* named oleo-palmito-butyrate of glycerol.

This was confirmed by the experiments of *A. W. Blyth* and *Robertson*,[1] who state that they isolated from butter fat a crystalline glyceride, to which they ascribed the formula



$$C_3H_5\begin{cases} O\,.\,C_4H_7O \\ O\,.\,C_{16}H_{31}O \\ O\,.\,C_{18}H_{35}O \end{cases}$$

Further experiments are required to resolve the apparently very complex mixture of glycerides in butter fat into its component parts. In the present state of our knowledge the method of practical crystallisation from solvents (cp. chap. xii. p. 417) offers the best hope of progress.

In order to prepare butter fat for the subsequent examinations, the sample of butter is melted in a porcelain dish at a temperature of about 50° C., until the upper layer has become perfectly clear. The supernatant fat is then decanted through a filter in the water oven.

It has been pointed out already that the adulteration of butter is nowadays practically confined to the admixture of foreign fats with butter fat, since gross adulterations with substances of a non-fatty nature are too easily detected.

In view of the fact that so many new methods for testing butter fat are being recommended, it should be emphasised that many chemists who publish new methods entirely seem to overlook the fact that there is not the slightest difficulty in distinguishing pure butter from margarine, or indeed from any other fat.

Before the methods of fat analysis had reached the completeness they possess to-day, margarine was very frequently sold—and is being sold to-day fraudulently—as butter.

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[1] *Proceed. Chem. Soc.* 1889, 5.

At present butter adulteration is practised on a most extensive scale by the admixture, in comparatively small proportions to the total fat, of foreign vegetable and animal fats, such as lard (goose fat), cotton seed stearine, cocoanut oil, palm nut oil, and chiefly margarine ("oleomargarine"). The last named fatty compound will be considered more fully under the heading of "Butter substitutes" in Chapter XV.

The frauds are being perpetrated on such extensive lines that legislation[1] has stepped in to protect the genuine article. In this country no butter-substitute, however small the proportion of foreign fat, may be sold without a distinct declaration as to its true nature.

The latest margarine law in Germany, as also in Austria, enacts that a manufacturer of margarine is bound to admix with the oils and fats employed 10 per cent of sesamé oil, for the sake of "ear-marking" such butter, as the recognition of sesamé oil is easy by means of the *Baudouin* test. This Act has, however, not been able to prevent the continuation of adulteration, since the importation of foreign made margarine, in the preparation of which no sesamé oil has been used, cannot be prevented.

The Belgian law demands the addition of 5 per cent of sesamé oil and 1 per cent of potato starch (reckoned on the fatty matter in the margarine). It also forbids the sale of abnormal butter.[2]

The difficulties that formerly attached to the detection of foreign fats in butter have been removed to a considerable extent by the modern methods of fat analysis. But the adulterator has kept pace with the progress of fat analysis, and has succeeded, with very great ingenuity, in preparing mixtures that can only be detected by a combination of several methods. Hence, judiciously prepared mixtures of margarine and cocoanut oil which formerly could not be detected by the saponification value and the Hehner value alone, are no longer admixed in considerable quantities with butter, since the application of the *Reichert-Meissl* (*Reichert-Wollny*) method immediately discloses the fraud. Yet such mixtures are still being used extensively in small quantities, since even the *Reichert-Meissl* test breaks down when 10 per cent of margarine are admixed with butter. Since the *Reichert-Meissl* value is a measure of the amount of volatile fatty acids, the writer expressed the fear in the first edition of this work that the artificial butter industry may succeed in providing means to prepare butter-substitutes having a correct *Reichert* value. This fear has been realised, since butyric acid, tributyrin, and also amyl acetate are being sold (in 40 per cent alcoholic solution) for that purpose, and patents have even been taken

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[1] A. Lavalle, *Die Margarine Gesetzgebung*, Bremen, 1896.—*Report of the Departmental Committee on Butter*, London, 1904.

[2] The law defines as abnormal, butter, the fat of which shows at least two of the following characteristics:—Scale divisions in the butyrorefractometer (at 40°) higher than 41 "degrees"; critical temperature of dissolution with alcohol of 99·1 per cent, a number exceeding 59° C.; specific gravity at 100° C., below 0·864; Reichert-Meissl value, below 25; Hehner value, above 89·5; and saponification value, below 221.

out[1] for the addition of volatile fatty acids to butter fat as also to margarine.[2] Such margarine will most likely find its way into butter, as its chemical characteristics only too plainly suggest fraudulent application, for the volatile acids may not only be used to improve the taste of the fatty material, as the patentees claim, but also to mislead the analytical chemist (cp. "Margarine," chap. xv.)

The application of the refractometric method has been of very great value in the rapid analysis of butter fats, especially for purposes of market control (see below). The adulterator has, however, been able to adapt himself also to this test and the difficulties of the analytical chemist have been enhanced lately by the employment of cocoanut oil in the adulteration of butter. Unfortunately, the practices of the adulterator are assisted to a very considerable extent by the natural fluctuations in the composition of the butter fat, since its chemical composition depends to a great extent on the breed of the cow, the mean temperature of the country where the butter is produced, the stabling, in short, the climatic influence to which the cows are exposed, further, on the nature and quantity of the food supplied, the period of lactation, and the idiosyncrasy of the individual cow. Notwithstanding the enormous amount of investigation that is being carried out in different countries, we are still unable to define the variations within which genuine butter fat may fluctuate. Some investigators followed the changes in the composition of butter fat obtained from a considerable number of cows, so as to eliminate the influence of one individual cow, whereas others (*Klein* and *Kirsten*) are of the opinion that only two factors, namely food and progress of lactation, are of importance, the other factors exercising a minor influence only, so that the examination of butter fats obtained from a limited number of animals may be considered sufficient. This, however, can hardly be admitted as correct, as the influence of stabling on the nature of butter has been shown to be so pronounced that during two different seasons of the year butter fats of very different composition are obtained from one and the same herd of animals.

Owing to the variations in the composition of butter fat, it is at present not possible to detect in every given case an admixture of 10 or even 20 per cent (in case the original butter was of very good quality) of foreign fats. The butter adulterator keeps therefore within the limits of such chemical tests as are from time to time agreed upon by analytical chemists, and hence prepares on a large scale adulterated butters which just keep near the lowest limits, so that the analyst is very frequently placed in the position of having to give to a butter the "benefit of the doubt" although he may feel convinced that adulteration has taken place. In case vegetable oils or fats have been admixed with butter in a direct manner, or, in an indirect manner, through added margarine,[3] the phytosteryl acetate test will give an unmistakable answer as to whether such admixture

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[1] E.P., 22,458, 1900; D.R.P., 121,657.

[2] E.P., 15,649, 1900.

[3] In the manufacture of which vegetable fats have been used.

has taken place or not. If, however, animal oils or fats are used as adulterants the uncertainty mentioned above still remains. In order to pronounce on the genuineness of a sample of butter, it is therefore necessary to combine several methods of examination. These methods will be enumerated in the order of their usefulness, and the influence which the different natural factors pointed out above have on the composition of the butter fat will be discussed under each heading.

The literature bearing on the examination of butter is an extraordinarily voluminous one, and still grows. The list of methods detailed below cannot therefore lay claim to completeness, although no important and really valuable method will be found missing. A large number of insignificant modifications of known methods and a host of valueless proposals have been deliberately omitted.

For further information reference must be made to special works on butter.[1]

REFRACTOMETRIC EXAMINATION

The first test that is usually applied is the determination of the refractive index of the butter fat by means of the butyro-refractometer or the oleo-refractometer; the butyro-refractometer will be found the handier instrument. Thus one is enabled to decide by a glance through the instrument whether a butter is grossly adulterated or whether it need only be regarded with suspicion. Owing to the rapidity with which this test can be carried out, its importance has been sometimes overestimated, and it should therefore be distinctly remembered that the refractometric test can only be used as a *sorting* test, and that its indications must be supported by further tests.

The refractive indices of pure butter fats have been given in the table, p. 835. An agreement as to which temperature should be adopted as the standard temperature for the refractometric observations has not yet been arrived at. Some observers choose 25° C., others again take 40° C.; the Government Laboratory has adopted 45° C. (the temperature employed by *Jean* in the observations with the oleo-refractometer).

All samples which give values lying outside the limits stated in the table must be looked upon as suspicious, or at least as "abnormal," and further examinations are required to establish whether a sample is pure or not.

In calculating the position of the critical line found in the butyro-refractometer at 25° C. for another temperature, a correction of 0·55 scale divisions should be made for each degree C.

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[1] Sell, *Arbeiten aus dem Kaiserl. Reichsgesundheitsamt*, 1886; Duclos, *Le Lait. Etude chimique et microbiologique*, Paris, 1887; Girard and Bevans, *La Margarine*, Paris, 1888; Besana, *Sui Metodi a distinguere il burro artificiale dal burro naturale*, Lodi, 1888; Zune, *Traité général d'analyse des beurres*, 2 vols., Paris et Bruxelles, 1892.—*Report of the Departmental Committee on Butter*, Eyre and Spottiswoode, London, 1904.

The following table, compiled on this basis, gives the practical limits for pure butter fats at the corresponding temperatures :—

Temperature. °C.	Scale Division.
25	52·5
26	51·9
27	51·4
28	50·8
29	50·3
30	49·8
31	49·2
32	48·6
33	48·1
34	47·5
35	47·0
36	46·4
37	45·9
38	45·3
39	44·8
40	44·2
41	43·7
42	43·1
43	42·6
44	42·0
45	41·5

Delaite,[1] however, has shown that numbers calculated from observations made at an arbitrary temperature are not identical with those directly observed. It is therefore necessary to make the observations at the desired temperature. 40° C. seems to be a suitable standard temperature.

If a sample furnishes numbers lying within the values given in the table p. 835, the conclusion must not yet be drawn that the sample is genuine. For mixtures of margarine and cocoanut oil can easily be prepared showing the refractive index of a normal butter fat. It is evident that any quantity of such mixture may be added to butter with impunity, in case the refractometric observations alone are held to give a decisive answer.

The assumption of earlier observers that the refraction of butter fat stands in a direct relation to the Reichert-Meissl (Reichert-Wollny) value, in other words, to the proportion of glycerides of volatile fatty acids (or, to be more correct, to mixed glycerides containing lower fatty acids), has not been borne out by recent evidence (cp. table, p. 859). It is quite true that (as in the last stages of the period of lactation [*Farnsteiner* and *Karsch* ;[2] *Masson*[3]], or in consequence of climatic conditions [*Holm*, *Kvarup*, and *Petersen*[4]]) the refraction increases with the decrease of volatile acids, but it has been shown abundantly that the refraction increases in a much

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[1] *Bullet. de l'Assoc. Belge de Chimistes*, 1894 (5), 145 ; *Analyst*, 1895, 95.

[2] *Zeit. f. Unters. Nahrgs. u. Genussm.* 1898, 16

[3] *Journ. Soc. Chem. Ind.* 1898, 861.

[4] *Biederm. Central.* 1901, 48.

greater ratio with the increase of unsaturated fatty acids; in other words, the higher the iodine value the higher will be the refraction. Such small influences on the refractive index as are caused by the higher proportion of volatile fatty acids are obliterated by the greater influence of the unsaturated fatty acids.[1] This is especially shown to be the case by butter fats obtained from cows fed on linseed cake (perhaps also cotton seed meal). Minute quantities of linseed oil pass into the milk, and consequently into the butter, as proved by the occurrence of linolenic acid in such abnormal butter fats. Therefore, as *Lobry de Bruyn* has shown first, Dutch butters are frequently met with giving deviations of – 25 to – 30, and even – 21 to – 26, in the oleo-refractometer, although they contained the normal amount of volatile fatty acids and had the proper flavour of good butter.

On the other hand, refractometer figures lying outside the numbers given in the tables do not unmistakably point to adulteration, but they certainly point to an "abnormal" butter. In these cases — as exemplified by "abnormal" Dutch butters[2] — further investigation must show whether the sample under examination is an adulterated butter or not.

Systematic investigations on the refraction of butter fats obtained from cows in different districts of the United Kingdom, and even from cows set apart for the purposes of an exhaustive inquiry, so that all the influences affecting the chemical composition of butter fat can be traced, were made by the Government Laboratory.[3] The observed fluctuations have been set out in the table, p. 835; they will be collated with their *Reichert-Meissl* (*Reichert-Wollny*) numbers in the tables to be given below.

The following two tables will be found of assistance in rapidly judging of the influence of adulterants on normal butters:—

Butyro-refractometer Observations at 25° C. (Wollny)

Kind of Fat.	Butyrorefractometer Scale Division.	Refractive Index n_D.
Genuine butters . .	49·5-54·0	1·4590-1·4620
Margarine	58·6-66·4	1·4650-1·4700
Mixtures of 1 and 2 . .	54·0-64·8	1·4620-1·4690

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[1] Cp. Partheil and v. Velsen, *Arch. d. Pharm.* 1900, 261.

[2] Cp. Lam. *Chem. Ztg.* 1900, 394.

[3] Thorpe, *Journ. Chem. Soc.* 1904, 248.

[TABLE

Oleorefractometer Observations at 45° C.

No.	Kind of Fat.	"Degrees."	Observer.
1	Margarine (Mouriès)	−14	Jean
2	"Crême Mouriès"	−15	,,
3	Oleomargarine	−17	,,
4	Pure butter with 10 % of No. 3	−28	,,
5	,, ,, 20 % ,,	−26	,,
6	,, ,, 30 % ,,	−25	,,
7	,, ,, 50 % ,,	−23	,,
8	Cotton stearine	+20	,,
9	"Vegetaline" (cocoanut butter)	−59	,,
10	Margarine	−13 to −18	Pearmain
11	Lard	− 8 to −14	,,
12	Tallow	−15 to −18	,,

The conclusion must therefore be accepted that the indications of the refractometer must be supported by other methods; in the first instance, by the determination of the *Reichert-Meissl* value.

THE REICHERT-MEISSL (REICHERT-WOLLNY) VALUE

The most valuable index in the chemical examination of butter fat is furnished by the determination of the *Reichert-Meissl* or *Reichert-Wollny* value. The *modus operandi* has been fully described in Chapter VI. p. 260. I omit a very large number of "new processes" which have been proposed from time to time, most of these processes being nothing but modifications and combinations of well-known methods. As an example of a superfluous method, I may mention *Kreis's* modification of *Reichert's* process, since it has met with greater attention than it actually deserves. *Kreis* employs for saponification concentrated sulphuric acid, but whereas on a large scale saponification is effected with 3 or 4 per cent of acid, *Kreis* uses no less than 10 c.c. for 5 grms. of butter fat. The experience of several chemists, including the writer, has proved that invariably sulphurous acid is liberated, which, of course, must vitiate the results unless the sulphurous acid is removed or otherwise rendered innocuous. The ingenuity of several analysts has been exercised to eliminate the error due to the presence of SO_2; others again have tried to exactly define the strength of the sulphuric acid required so as to avoid formation of sulphurous acid.

In order to avoid the possibility of the formation of ethylic esters in the saponification process, *Leffmann* and *Beam* proposed to saponify by means of caustic soda and glycerin. It has been shown above (chap. ii.) that, provided a sufficient amount of alkali be used, ethylic esters cannot be formed. But since this process has been adopted by several laboratories affiliated to dairies and by the German Imperial "Gesundheitsamt," it may be described here.[1] Mix 20 c.c. of a solution

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[1] Cp. *Analyst*, 1896, 259.

of 100 grms. of caustic soda[1] in an equal weight of water with 180 c.c. of pure concentrated glycerin. Weigh 5 grms. of the filtered fat into an Erlenmeyer flask, add 20 c.c. of the alkali solution, and heat over a naked flame for two or three minutes until the water is driven off and the liquid becomes clear.

From the analyses of many thousands of samples of butter fat the fact has been deduced that the Reichert value is by no means so constant as *Reichert's* researches have led to believe, the quantity of volatile acids being influenced to a notable extent by the nature of the food, the seasons, the period of lactation, the method employed in melting the butter, its state of freshness (rancidity), etc.

In the following table I have collated the *Reichert-Meissl* (*Reichert-Wollny*) values published by a number of observers, the *Reichert* values (for 2·5 grms.) having been multiplied by 2·2 so as to admit of a comparison with the *Reichert-Meissl* (*Reichert-Wollny*) values, although this procedure is, strictly speaking, not correct. But as the variations in the numbers of butter fats are greater than the error involved by the employment of a necessarily inaccurate factor, the table will be found sufficiently useful for practical purposes.

Reichert-Meissl (*Reichert-Wollny*) *Values of Butter Fat*

Origin.	Number of Samples.		c.c. decinormal KOH.	Observer.
English		?	31·9	Muter.
		7	27·6 – 29·2	Vieth.
	357	7	22·5	Thorpe.
		17	23·5	,,
		15	24·5	,,
		27	25·5	,,
		37	26·5	,,
		51	27·5	,,
		78	28·8	,,
		56	29·5	,,
		41	30·5	,,
		18	31·3	,,
		10	32·6	,,
Dutch—during September, October, November, December	428	3	17 – 18·9	van Rijn.[2]
		3	19 – 19·9	,,
		8	20 – 20·9	,,
		28	21 – 21·9	,,
		34	22 – 22·9	,,
		64	23 – 23·9	,,
		74	24 – 24·9	,,
		56	25 – 25·9	,,
		67	26 – 26·9	,,
		43	27 – 27·9	,,
		34	28 – 28·9	,,
		9	29 – 29·9	,,
		5	30 – 33	,,

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[1] Wrampelmeyer (*Landw. Vers. Stat.* 1897, 49, 215) states that caustic potash and glycerin give unsatisfactory results ; it is, however, difficult to see why this should be so.

[2] *On the Composition of Dutch Butter*, London, 1902. Cp. also Reicher, *Zeit. ang. Chem.* 1901, 125 ; Clark, *Analyst*, 1901, 113 ; *Report of the Departmental Committee on Butter*, Eyre and Spottiswoode, London, 1894.

Reichert-Meissl (*Reichert-Wollny*) *Values of Butter Fat* (continued)

Origin.	Number of Samples.	c.c. decinormal KOH.	Observer.
Oct. 17, 1900-Sept. 4, 1901—	632[1]		
Minimum, in November	...	22·1	van Rijn.
Maximum, in March	...	33·4	,,
Danish—			
Minimum	...	20·0	
Maximum	...	33·0	
Swedish	22	26·9 – 29·4	Vieth.
	797	22·9 – 41·0	Nilson.
Norwegian—			
Nov. 1898 to Dec. 1901—	657[1]		
Minima, in June	...	21·1	
,, in March	...	28·6	
Maxima, in August	...	31·2	
,, in January	...	34·9	
German	?	30·8	Reichert.
	?	27·0 – 31·5	Meissl.
	?	27·6 – 29·4	Reichardt.
	?	24 – 32·8	Sendtner.
	?	22-32	Thoerner.
North-West Germany—			
Dec. 1898 to Nov. 1899—			
Minima, in Oct.-Nov.	...	22·8 – 24·9	Vieth.
Maxima, in April-June	...	29·1 – 31·3	,,
Dec. 1899 to Nov. 1900—			
Minima, in Oct.-Nov.	...	22·4 – 24·6	,,
Maxima, in April-May	...	29·9 – 31·0	,,
French	?	29·26	Jean.
	28	26·1 – 30·6	Vieth.
	39	26·9 – 30·8	,,
Belgian	693	26 – 36·85	Wauters.
	26	25 – 25·84	,,
	16	24 – 24·96	,,
	9	23·08 – 23·84	,,
	11	19·8 – 23	,,
Italian	178	26·1 – 31·4	Corbetta.
Minima	?	20·63	Spallanzani.
	?	19·8	Spallanzani and Pizzi.
	?	20·68	Vigna.
	?	21·56	Maissen and Rossi.
	?	21·80	Besana.
	?	22·55	Longi.
	?	23·59	Sartori.
Maximum	?	30·14	Spallanzani and Pizzi.

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[1] From fifty-three factories.

Reichert-Meissl (Reichert-Wollny) Values of Butter Fat (continued)

Origin.	Number of Samples.	c.c. decinormal KOH.	Observer.
Russian—			
Minimum, in July .	...	25·7	Lewin.
Maximum, in February	...	30·5	,,
October-January . .	161	...	Russian Bacteriological Laboratory
Minimum, in November	...	21·89	,, ,,
Maximum, in January .	...	27·3	,, ,,
Minimum, in April .	74	20·4	St. Petersburg City Laboratory
Maximum, in February	...	30·3	,, ,,
Siberian—			
Minimum . . .	...	24·6	Lewin.
Minimum, in April .	150	24·0	Russian Bacteriological Laboratory
Maximum, in August .	...	30·7	,, ,,
Swiss.	?	28·10 – 31·10	Ambühl.
American	?	27·36	Cornwall and Wallace.

From the foregoing table it will be gathered that the Reichert-Meissl (Reichert-Wollny) values of butter fats vary considerably in different countries, and with the different seasons of the year. It may appear somewhat unjust to fix a minimum limit; still, in order to prevent, to some extent at least, the fraud that would be practised if the Reichert-Meissl (Reichert-Wollny) value were allowed to fall below a certain number, the minimum value for a genuine butter generally adopted amongst analysts, although not officially, in this country and France is 24, in Germany 25, and in Sweden 23. An enormous amount of evidence has been published[1] to show that under certain conditions—which will be discussed below—the Reichert-Meissl value of genuine butter fat may fall, and, indeed, does fall below these limits. But it has been also proved that with proper methods of dairying and with proper feeding and stabling, even under severe climatic conditions, the characteristic amount of volatile acids, as expressed by the Reichert number, does not vary much, and it would therefore appear unwise to reduce those adopted limits on the strength of individual, mostly exceptional, cases. Such a procedure would undoubtedly lead to greater laxity on the part of the producers of butter. It may be objected, and indeed has been objected, that by fixing a low limit, such as 23, the adulterator would be in a position to regulate his admixtures to some extent so as to keep at as low a limit as possible. This might be met by raising the limit, but it should be remembered that the skilled

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[1] Cp. *Report of the Departmental Committee on Butter*, Eyre and Spottiswoode, 1904.

adulterator will in any case adapt himself to given conditions. At present enormous quantities of butter are sold in this country the fat of which gives Reichert-Meissl values of exactly 24. Nor should greater scope be given to what has been termed by *Meissl* "adulteration through the cow," caused by bad feeding, or by not stabling the cows when the cold season sets in, or other conditions which influence the quality of the butter. This may be illustrated at the instance of Dutch butters. It has been shown[1] that butter made in the northern provinces of Holland during October shows lower Reichert-Meissl values than butters produced on the one hand in September, and on the other hand during November and December. The cause of this decrease in the amount of volatile fatty acids is due to the climatic conditions obtaining during October; after the cows have been stabled in November, the amount of volatile fatty acids again increases.

It is being contended that there exists no connection between the quality of butter and its chemical composition, and that a butter need not be of inferior quality because it contains a low percentage of volatile fatty acids. *Lewin*[2] objects to this assertion, but even if this point be left an open question, it cannot be denied that to fix the limits too low, or to fix no limit, would be to take out of the hands of the analyst his best weapon against the adulterator and the careless farmer. Since butter from the southern provinces of Holland, where the cows are stabled almost throughout the year at nights, shows no such falling off in the amount of volatile fatty acids, it would follow that the butter manufacturer has it in his power to keep up to a standard which, for want of better analytical methods, may legitimately be considered a just and equitable one.

Similar conditions to those described above obtain in North-West Germany (*Vieth*[3]) and in Siberia;[2] in fact they may be shown to occur in any country; therefore butter falling below the limit of 24 (Reichert-Wollny number) should be considered "abnormal," if further investigation proves that no adulteration with foreign fats has taken place.

The nature of the *food* also greatly influences the amount of volatile fatty acids. *Spallanzani* and *Pizzi*[4] have shown that when cows are out to grass the butter is rich in volatile acids, which diminish when the cows are stall fed on a *poor* ration.

This agrees with *Swaving's* experience that in the beginning of the grazing season the volatile acids increase, remaining at a high figure until the close of the season.

If cows are fed on oil cakes, the Reichert-Meissl value of the fat decreases considerably, in consequence of the oil passing into the milk fat. Thus it has been shown that cows fed with cotton

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[1] Van Rijn; Reicher.

[2] Cp. *Report of the Departmental Committee on Butter*, Eyre and Spottiswoode, 1904.

[3] *Milch Zeitung*, 1901, No. 12.

[4] *Staz. Sper. Agrar. Ital.* 38, 257.

seed cakes yield butter fats of higher melting point (cp. table, p. 836), with a corresponding decrease of about 1 per cent of volatile fatty acids. (It has been mentioned already that butter fat from cows fed with linseed cakes behaves abnormally in the refractometric examination.[1]) *Baumert* and *Falke*[2] especially have shown that on feeding cows with oil cakes, butter fats are obtained which exhibit *Reichert-Meissl* values corresponding to an artificial mixture of butter fat with the oils contained in the cakes. Butters of this kind should at least be looked upon as "abnormal" butters or as inferior in quality. (A manufacturer who carries out admixture by means of dead machinery in a works would certainly be termed an adulterator!)

The variation of the Reichert-Meissl value with the *season* is clearly brought out by the following numbers, due to *Vieth*:[3]—

London-made Butter.	Reichert-Meissl Value.
From July 30 to November 12, 1889	25·8-27·1
From March 25 to June 24, 1890	27·2-30·0

Great fluctuations in the composition of butter fat are caused by the *period of lactation*. *Nilson* has shown in the case of Swedish butter that the *Reichert-Meissl* value decreases from 33·44 in the first month to 25·42 in the fourteenth month of lactation. According to *Vieth*, Holstein butter, made at a time when most of the cows were nearing the end of the period of lactation, gave numbers as low as 21·7; also *Spallanzani* and *Pizzi* and a number of other observers find higher *Reichert-Meissl* values in the early stages of lactation than in the later ones. [*Swaving*,[4] indeed, goes so far as to consider on this account 14 as the permissible minimum.] Similar depressions occur during the rut-time and illness of the cows.

Excellent as *Reichert's* method is, sophistication with 20 per cent of a foreign fat in the case of butters rich in volatile acids, or of 10 per cent in the case of butters of ordinary quality, cannot be detected with certainty in every case. Still, *Reichert's* process must be considered the best method hitherto designed for the detection of frauds, or of "abnormal" butters, no other method allowing rapid discrimination between genuine butter and a butter adulterated with a judiciously prepared mixture of margarine and cocoa nut oil. The following table demonstrates this clearly:—

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[1] Cp. Lindsay, *Massachussetts Stat. Rep.* 1900. 14.

[2] Cp. also A. Ruffin, *Ann. de Chim. Anal.* 1899, iv. 383.

[3] *Journ. Chem. Soc.* 1891, 508.

[4] *Landw. Versuchsstat.* 1891, 127.

[TABLE

Reichert-Meissl Values

Kind of Fat.	c.c. decinormal Potash.	Observer.
Cocoa nut oil	7·0-7·8	Reichert, Moore, Allen, Muter
Margarine	2·6	Muter
Oleomargarine	0·8-0·9	Jean
Butter fat with 10 per cent of cocoa nut oil .	26·8	,,
,, ,, 20 ,, ,, ,, .	24·13	,,
,, ,, 25 ,, ,, ,, .	24	Muter
,, ,, 50 ,, ,, ,, .	18	,,
,, ,, 75 ,, ,, ,, .	12	,,
50 parts of butter fat, 22·5 parts of cocoa nut oil, and 27·5 parts of oleomargarine . .	17·4	Moore

Only in those cases where margarine alone has been used for adulteration, and its proportion exeeds 10 per cent, will the determination of the saponification value be more expeditious. A butter fat containing more than 10 per cent of margarine gives a low saponification value (see below). In doubtful cases it is therefore advisable to determine the saponification value as well as the Reichert-Meissl value. Thus, in case butyric acid, butyrin, or amyl acetate have been added to conceal an admixture of margarine, an abnormally high saponification value in conjunction with a normal Reichert-Meissl value will lead to their detection. Furthermore, whenever an abnormally high saponification value is associated with an abnormally low Reichert value, the presence of cocoa nut oil may be suspected.

The following table presents several examples of those cases where the Reichert-Meissl value just reaches the figure 24, and the analyst is therefore confronted with uncertainty as to whether the butter is adulterated or not :—

[TABLE

No.	Fat.	Reichert-Meissl Value.	Oleo-Refractometer.	Observer.
			Deviation.	
1	Genuine butter	26-29	– 30	Jean
	,, ,, ...	31·9	– 34	Muter[1]
2	Cocoa nut oil	7-8	– 59	Jean
	,, ,, ...	7·7	- 54	Muter
3	Genuine butter with 10 per cent of cocoa nut oil	26·8	– 33	Jean
4	,, ,, ,, 15 ,, ,, ,,	...	– 34	,,
5	,, ,, ,, 20 ,, ,, ,,	24·13	– 36	,,
6	,, ,, ,, 25 ,, ,, ,,	26·4	– 39	Muter
7	,, ,, ,, 50 ,, ,, ,,	19·8	– 44	,,
8	,, ,, ,, 75 ,, ,, ,,	13·2	– 49	,,
9	Margarine	2·8	– 8·5	,,
10	Genuine butter with 25 per cent of margarine	24	– 27	,,
11	,, ,, ,, 50 ,, ,,	17·1	– 22	,,
12	,, ,, ,, 75 ,, ,,	9·9	– 15	,,
13	Margarine with 50 per cent of cocoa nut oil .	6·1	– 32	,,
14	50 per cent genuine butter with 25 per cent of margarine and 25 per cent of cocoa nut oil .	19·3	– 33	,,
15	25 per cent genuine butter with 50 per cent of margarine and 25 per cent of cocoa nut oil .	12·3	– 27	,,

The specimens represented by Nos. 3 and 4 of the foregoing table cannot be reported as adulterated samples if judged by the Reichert-Meissl value and by the refractometric method alone.

The adulterator has taken advantage of this fact, and hence during recent years—especially in Belgium—large amounts of butter are undoubtedly being adulterated with cocoa nut oil.

In cases of this kind, the **phytosteryl acetate test** leads unmistakably to the detection of vegetable oils.

Since this test demands a considerable amount of time, as well as of material, the detection of cocoa nut oil by *Polenske's* method may be resorted to.

The principle underlying his method rests on the fact that by far the greater part of the volatile fatty acids of *butter fat* obtained in the Reichert distillation process is soluble in water, a small quantity only being insoluble, whereas in the case of *cocoa nut oil*, a small amount only of the volatile acids obtained by the Reichert distillation process is soluble in water, by far the largest amount being insoluble. By titrating these two kinds of fatty acids with decinormal potash separately, a great difference between butter fat on the one hand and cocoa nut oil on the other will be established. This difference can also be traced in butters adulterated with comparatively small quantities of cocoa nut oil, say about 10 per cent. This principle has been made use of by *Hart*,[2] *Wauters*,[3] *Vandam*,[4]

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[1] The Reichert values given by *Muter* have been multiplied by 2·2 for the sake of better comparison.

[2] *Chem. Zeit.* 1901, 207.

[3] *Bull. de l'Assoc. Belge des Chim.* 1901, 258.

[4] *Ann. de Pharm. de Louvain*, 1901, 201.

and *Reychler.*[1] Thus *Wauters* required (on applying his method of distilling twice) 11·4 c.c. of decinormal potash, for the soluble volatile acids of cocoa nut oil and 15·4 c.c. for its insoluble volatile acids, whereas several samples of butter fat (taking the mean of three samples) required 27·9 c.c. for the soluble volatile acids and 0·9 c.c. for the insoluble volatile acids.

Although the details of *Wauters'* process have been criticised by *Ranwez*,[2] the underlying principle is a sound one (cp. also *Jean* [3]). It has been carefully worked out to a new method for determining cocoa nut oil in butter by *Polenske.*[4]

Polenske ascertained, by examining thirty-one samples of butter fat, the *Reichert-Meissl* values of which varied from 23·3 to 30·1, that the amount of c.c. of decinormal alkali required for the insoluble volatile fatty acids varied from 1·5 to 3·0 c.c., whereas in the case of 4 samples of cocoa nut oil having the Reichert-Meissl values 6·8 to 7·7, as much as 16·8 to 17·8 c.c. of decinormal potash were required for the neutralisation of the insoluble volatile acids. (The number of c.c. of decinormal alkali required for the neutralisation of the *insoluble* volatile fatty acids is termed by *Polenske* "new butter value.") *Polenske* further lays stress on the fact that the insoluble volatile fatty acids of butter fat form oily drops, if the Reichert-Meissl value of the butter fat be low, or a semi-solid, non-transparent mass in case the Reichert-Meissl value be high. He further observed that if to butter fat 10 or more per cent of cocoa nut oil be admixed, the insoluble volatile acids no longer solidify. (This is explained by *Polenske* by the fact that the volatile acids of cocoa nut oil contain large quantities of caprylic acid, whereas in the case of butter fat capric acid predominates.) *Polenske's* method is in its first stage almost identical with the Reichert method. A large number of experiments have demonstrated that it is absolutely necessary to follow the process in all its minutest details, in order to obtain concordant results.

Polenske saponifies 5 grms. of filtered butter fat, by the *Leffmann-Beam* process, with 20 grms. of glycerin and 2 c.c. of caustic soda solution (prepared from equal parts of sodium hydrate and water) in a 300 c.c. flask by heating over a free flame. The solution is allowed to cool below 100°, 90 c.c. of water are added, and the mass dissolved by warming on the water-bath to about 50° C. The solution must be clear and almost colourless. In case a brown solution be obtained, the test must be rejected. To the hot soap solution 50 c.c. of dilute sulphuric acid (containing 25 c.c. of pure concentrated sulphuric acid in 1000 c.c.) and some powdered pumice are added; the flask is then immediately attached to the condenser. The apparatus to be employed must correspond in all details to the dimensions given in Fig. 61. The heat must be so regulated that within 19 to 20 minutes 110 c.c. are distilled off; the cooling water

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[1] *Bull. de la Soc. Chim.* 1901, 142.

[2] *Ann. Pharm.* 1901, 241. Cp. Van Leent, *Chem. Centr. Blatt.* 1903, ii. 1193.

[3] *Annal. Chim. Anal. Appl.* 1903, 441.

[4] *Arbeit. aus dem Kaiserl. Gesundheitsamte*, 1904, 545.

must be supplied at such a rate that the distillate does not drop at a higher temperature than 20°-23° C. into the 110 c.c. flask. As soon as 110 c.c. have distilled over, the flask is removed, and replaced by a 20 c.c. measuring cylinder.

The distillate, which must not be shaken through, is immersed almost completely into water of 15° C. After about five minutes the neck of the flask is slightly tapped so that the oil-drops floating on the surface may adhere to the walls of the flask. After further ten minutes the consistence of the insoluble acids is noted, with a view to ascertaining whether they form a solid (semi-solid) mass or oily drops. The contents of the flask are then mixed by turning the corked flask four or five times upside down, avoiding, however, violent shaking, and 100 c.c. are filtered off through a filter of 8 cm. diameter, and titrated with decinormal caustic potash, as is done in the determination of the Reichert-Meissl value. In order to remove the soluble acids completely, the filter is washed three times in succession with 15 c.c. of water, which have been passed severally through the tube of the condenser, the 20 c.c. measuring cylinder, and the 110 c.c. flask. The tube of the condenser, the measuring cylinder, and the 110 c.c. flask are then washed in the same manner three times successively with 15 c.c. of neutralised 90 per cent alcohol, each quantity being allowed to drain before a fresh wash is poured on the filter. The alcoholic filtrate is then titrated with decinormal alkali.

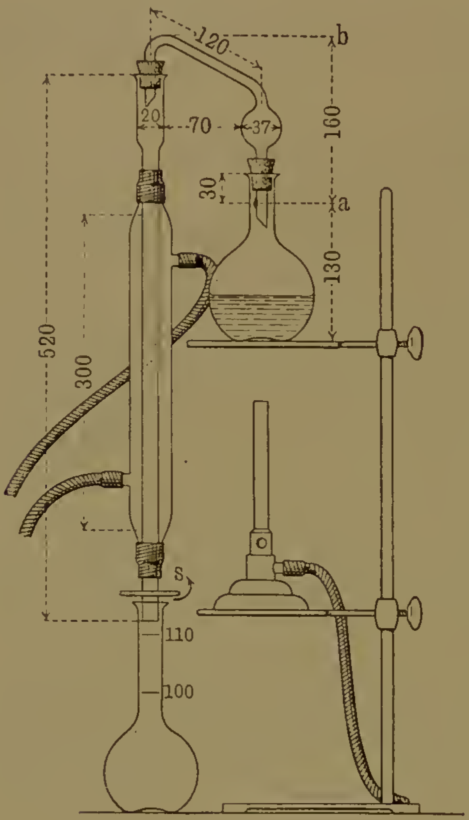

Fig. 61.

In the following table I reproduce a number of values published by *Polenske* for pure butter fats, and the same butter fats after they have been admixed with 10 per cent, 15 per cent, and 20 per cent of cocoa nut oil respectively:—

[TABLE

No.	Number of c.c. $\frac{1}{10}$ norm. KOH required for the Neutralisation of the							
	Soluble Volatile Acids (R.M. Value).	Insoluble Volatile Acids.	Soluble Volatile Acids (R.M. Value).	Insoluble Volatile Acids.	Soluble Volatile Acids (R.M. Value).	Insoluble Volatile Acids.	Soluble Volatile Acids (R.M. Value).	Insoluble Volatile Acids.
	of Pure Butter Fat.		of Same Butter Fat containing 10 per cent of Cocoa Nut Oil.		of Same Butter Fat containing 15 per cent of Cocoa Nut Oil.		of Same Butter Fat containing 20 per cent of Cocoa Nut Oil.	
1	19·9	1·35	18·7	2·4	18·1	2·9	17·6	3·3
2	21·1	1·4	19·7	2·3	19·2	3·0	18·5	3·6
3	22·5	1·5	21·0	2·5	20·4	2·9	19·8	3·5
4	23·3	1·6	22·0	2·5	21·5	3·1	21·0	3·7
5	23·4	1·5	22·3	2·4	21·7	3·1	21·2	3·7
6	23·6	1·7	22·5	2·5	21·9	3·3	21·4	4·0
7	24·5	1·6	23·3	2·5	22·4	3·1	21·7	3·7
8	24·7	1·7	23·8	2·9	22·9	3·5	22·1	3·9
9	24·8	1·7	23·5	2·7	22·7	3·2	...	...
10	24·8	1·6	23·4	2·5	22·8	3·0	22·1	3·6
11	25·0	1·8	23·0	2·7	23·3	3·1	21·8	3·6
12	25·1	1·6	23·5	2·5	23·1	3·0	22·5	3·8
13	25·2	1·6	23·4	2·6	22·9	3·0	22·3	3·7
14	25·3	1·8	24·0	2·9	23·5	3·5	22·6	4·1
15	25·4	1·9	24·2	3·0	23·7	3·6	22·6	4·1
16	25·6	1·7	24·1	2·7	23·3	3·1	22·7	3·7
17	25·4	1·7	23·8	2·6	23·0	3·1	...	...
18	26·2	1·9	25·0	3·1	24·2	3·6	23·6	4·0
19	26·5	1·9	25·0	2·9	24·1	3·5	23·2	4·1
20	26·6	1·8	25·4	2·9	24·6	3·3	23·9	3·8
21	26·7	2·0	25·2	3·2	24·5	3·6	23·7	4·2
22	26·8	2·0	24·8	3·0	24·2	3·4	23·5	4·0
23	26·9	2·1	25·2	2·9	24·1	3·6	23·2	4·2
24	26·9	1·9	24·9	2·9	24·0	3·3	23·3	4·0
25	27·5	1·9	25·7	2·7	24·9	3·3	24·0	3·9
26	27·8	2·2	26·0	3·1	25·0	3·7	...	...
27	28·2	2·3	26·1	3·1	25·1	3·8	24·5	4·4
28	28·4	2·3	26·5	3·5	25·7	4·0	25·1	4·5
29	28·8	2·2	26·8	3·3	26·0	3·9	...	...
30	28·8	2·5	27·1	3·5	26·3	4·0	25·4	4·7
31	29·4	2·6	27·6	3·8	26·9	4·2	...	...
32	29·6	2·8	27·5	3·8	26·2	4·2	25·5	4·9
33	29·5	2·5	27·4	3·5	26·6	4·1	25·4	4·7
34	30·1	3·0	27·8	3·8	26·9	4·4	26·2	5·0

With the assistance of this table *Polenske* claims to be able to calculate quantitatively (though only approximately) the admixed amount of cocoa nut oil in an adulterated butter fat, relying on the conclusion to be derived from the given numbers, viz. that the amount of alkali required for the neutralisation of the insoluble volatile acids is increased by 0·1 c.c., through the addition of 1 per cent of cocoa nut oil. An example may illustrate his manner of calculation :—Suppose a sample of butter fat gave the Reichert-Meissl value 24·5, and required for the neutralisation of the insoluble volatile fatty acids 3·0 c.c. of decinormal alkali.

The insoluble volatile acids were found to be liquid. According to the foregoing table, a *pure* butter fat of the Reichert-Meissl value 24·5 requires only 1·6 c.c. of decinormal alkali for the neutralisation of the insoluble volatile acids; hence, there was used an excess of 3·0 – 1·6 = 1·4 c.c. for the neutralisation of the insoluble volatile fatty acids. The sample must therefore be judged to have been adulterated with cocoanut oil. Since each 0·1 c.c. is taken to correspond to 1 per cent of added cocoa nut oil, the sample would contain 14 per cent of cocoa nut oil. Examples 15 and 22 of the foregoing table (24·2; 3·0 and 24·8; 3·0) would point to an admixture of 10 per cent of cocoa nut oil. The sample which gave these numbers actually did contain 10 per cent of cocoa nut oil.

Although this method must be considered a valuable addition to the armoury of the analytical chemist, it should not be overlooked that some uncertainty still adheres to it,[1] especially as regards its quantitative interpretation, since the value of this method can be rendered nugatory by the employment of smaller quantities of cocoa nut oil than 10 per cent, or of a mixture of cocoa nut oil and margarine. This method supplements, however, the *phytosteryl acetate test*, which in its present form does not admit of quantitative interpretation, and obviously becomes useless in case a margerine "earmarked" with sesamé oil or containing other vegetable oils and fats has been employed.

If in the *absence* of vegetable fats Reichert-Meissl values are obtained which leave a doubt as to the genuineness of the butter, then admixture of *animal* fats only can be suspected. In that case corroborative evidence should be sought in the determination of the specific gravity.

Specific Gravity

From the tables giving the specific gravities of fats free from glycerides of soluble fatty acids, and fats containing glycerides of soluble fatty acids (pp. 170-171), it will be gathered that the specific gravity test can be used in conjunction with other tests as a critical test in the examination of butter fats.

J. Bell, who first proposed the specific gravity test for the examination of butter fat, chose the temperature of 100° F. = 37·8° C., and used an ordinary pear-shaped specific gravity bottle. In the examination of a large number of samples he found that the experimental values vary within the narrow limits of 0·911 and 0·913. In the subjoined table I collate the specific gravities of genuine butter fats and some other fats likely to be used as adulterants, determined at a temperature of 100° F.

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[1] Cp. also Juckenack's and Pasternack's table, p. 860.

Kind of Fat.	Specific Gravity at 100° F. =37·8° C. (water at 37·8=1).	Observer.
Genuine butter fat, 113 samples	0·911-0·913	Bell
,, ,, ,, 357 ,,	0·9101-0·9130	Thorpe
Mutton suet	0·90283	Bell
Beef suet	0·90372	,,
Oleomargarine	0·90136-0·90384	,,
Cocoa nut oil	0·9167	Moore

From the last table, as also from the table given on p. 171, the fact will be gathered that cocoa nut and palm nut oils, if present in small quantities, cannot be detected by the specific gravity test alone. It further follows that a judiciously prepared mixture of cocoa nut oil with animal oils can be incorporated with butter fat without being detected by an abnormal specific gravity number. This qualifies *Violette's*[1] statement that by means of a density determination alone butters may be rapidly sorted into three classes, viz. (*a*) those undoubtedly adulterated with margarine, arachis, sesamé, and poppy seed oils; (*b*) those open to suspicion; (*c*) those that may be considered practically pure.

Nothing is therefore gained by calculating the specific gravity to the weight *in vacuo* as *Violette* proposes. His numbers may, however, be recorded here :—

1 c.c. of	At 100° C. weighs *in vacuo.* Grms.
Genuine butter fat	0·86328-0·86425
Margarine	0·85766-0·85865

Skalweit, having found that the differences in the specific gravities of butter fats and fats likely to be used as adulterants are greatest at 35° C., prefers this temperature. His observations are given in the following table :—

Temperature.	Lard.	Margarine.	"Butterine."	Butter Fat.
°C.				
35	0·9019	0·9017	0·9019	0·9121
50	0·8923	0·8921	0·8923	0·9017
60	0·8859	0·8857	0·8858	0·8948
70	0·8795	0·8793	0·8793	0·8879
80	0·8731	0·8729	0·8728	0·8810
90	0·8668	0·8665	0·8663	0·8741
100	0·8605	0·8601	0·8598	0·8672

Other chemists prefer to determine the specific gravity at 100° C. (water of 15° C. = 1); the results recorded by the different observers agree in a satisfactory manner :—

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[1] *Journ. Soc. Chem. Ind.* 1894, 54.

Fat.	Koenigs.	Sell.	Allen.
			At 99° C., water 15·5 = 1.
Genuine butter fat	0·866-0·868	0·866-0·868	0·867-0·870
Beef tallow	...	0·859-0·8605	
Lard	...	0·860-0·8605	
Oleomargarine	...	0·859-0·860	0·8585-0·8625
Adulterated butter	0·859-0·865		
3 parts of genuine, 1 part of artificial butter	...	0·865	
1 part of genuine, 1 part of artificial butter	...	0·863-0·864	

The specific gravities at 100° C., referring to water of 100° C. as unit, are tabulated here—

Specific Gravities at 100° C., *Water at* 100° C. = 1

Fat.	J. Bell.	Muter.	Allen.
Genuine butter fat	0·9094-0·9140	0·9105-0·9138	0·9099-0·9132
Oleomargarine	0·9014-0·9038	0·903-0·906	0·902-0·905

Through the introduction of the Reichert method, older processes, such as the determination of the saponification value and of the insoluble fatty acids, as also the determination of the mean molecular weights of the non-volatile acids (cp. table below), have at present become of secondary importance, since the indications furnished by these two tests are implicitly given by the *Reichert* test. They can, therefore, only be considered briefly.

SAPONIFICATION VALUE

As indicated in the table (p. 834) the mean saponification value of butter fat may be taken as 227.

Butter fats that yield abnormal *Reichert-Meissl* values also give abnormal saponification values, so that, to take an example, the saponification value may drop in the last stages of lactation to 218·5. It need not be repeated here that the saponification value alone is no proof of purity, for it is very easy to prepare mixtures of oleomargarine and cocoa nut oil having the mean saponification value of 227. The saponification value is best collated with the Reichert value. It has been shown above that when an abnormally high saponification value is associated with a low Reichert value the presence of cocoa nut oil may be suspected.

Hehner Value

Hehner showed that the proportion of insoluble acids plus unsaponifiable in genuine butter fats varies from 86·5 to 87·5 per cent, reaching sometimes 88 per cent.

Since some butter fats contain considerable quantities of lauric acid, too high values may be found unless the directions given above for washing the fatty acids (p. 263) be followed. The limits for the *Hehner* value obtained by other experimenters are given in the subjoined table:—

Hehner Values of Butter Fat

Observer.	Per cent Insoluble Acids.	
	Lower Limit.	Upper Limit.
J. Bell	85·5	87·9
Fleischmann and Vieth .	85·79	89·73
West-Knight . . .	...	88·08
Thorpe (357 samples) . .	87·7	90·1

Butter fats, the *Hehner* value of which exceeds 90, must be looked upon as adulterated or "abnormal." Normal numbers are, of course not absolute proof of the purity of a sample, as in the case of the fat from cows in the last stages of lactation high values are found.

A synopsis of a number of determinations carried out with 357 samples of English butter fats (*Thorpe*[1]) is reproduced in the following table:—

I.	II.	III.	IV.	V.	VI.	VII.
No. of Samples.	Butyro-refractometer at 45° C.	Reichert-Wollny Value.	Specific Gravity at $\frac{37{\cdot}8^\circ}{37{\cdot}8^\circ}$ C.	Saponification Value.[2]	Insoluble Acids. Per Cent.	Mean Molecular Weight of Insoluble Acids.
7	42·0	22·5	0·9101	219·65	90·1	266·9
17	41·5	23·5	0·9104	221·39	89·7	265·5
15	41·5	24·5	0·9108	223·24	89·4	265·0
27	41·3	25·5	0·9110	223·41	89·3	264·2
37	41·0	26·5	0·9113	225·39	88·9	261·9
51	40·6	27·5	0·9114	226·75	88·7	261·7
78	40·1	28·8	0·9118	228·32	88·4	260·9
56	40·1	29·5	0·9120	229·91	88·3	259·6
41	39·9	30·5	0·9123	231·43	87·9	260·1
18	39·7	31·3	0·9125	232·30	87·9	258·0
10	39·4	32·6	0·9130	232·58	87·7	257·8
357						

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[1] *Journ. Chem. Soc.* 1904, 254.

[2] Calculated by me from the saponification-equivalents given by Thorpe.

This table may be supplemented by the following table given recently by *Juckenack* and *Pasternack.*

	Reichert-Meissl Value.	Saponification Value.	Mean Molecular Weight of Insoluble Acids.	Number of c.c. decinormal KOH required for the neutralisation of the Insoluble Volatile Acids (*Polenske's* method).
Pure Butter fat . . .	27·5	223·4	260·2	1·80
,, ,, +10% Cocoa nut oil	25·3	226·9	254·1	2·85
,, ,, +20% ,,	24·1	230·2	249·0	4·30

The *iodine value* is of very little importance in the examination of butter fats. This is shown in the first instance by the great variations in the numbers recorded in the table, p. 834. The amount of unsaturated fatty acids in a butter fat is greatly influenced by the kind of oil or fat given with the food. Since the amount of unsaturated fatty acids influences the refractometric constant, the indications furnished by the iodine value are implicitly given by the refractometer numbers of the sample.

It should further be added that all those influences which tend to reduce the amount of volatile fatty acids, apart from the influence of food, naturally increase to some extent the iodine value. Thus *Farnsteiner* and *Karsch* found the iodine value of butter fat obtained from cows that had been in milk for a long time as high as 49·7.

If it be desired to ascertain whether vegetable oils have been introduced into an adulterated butter (with the help of margarine), then the *phytosteryl acetate test* will give the information in an unmistakable manner.

Special colour reactions for vegetable oils are hardly required in the examination of butter fat, and should only be used as corroborative tests. It should, however, be remembered that a positive Halphen test given by a butter fat does not prove the presence of cotton seed oil, since the chromogenic body giving the Halphen reaction passes into the milk fat of cows fed on cotton seed cake.

It has been proved (*Baumert* and *Falke, Thorpe*[1]) that the chromogenic body giving the Baudouin reaction does not pass into the milk fat of cows fed on sesamé cake. Hence a positive Baudouin reaction may indirectly prove adulteration with a margarine, in the manufacture of which sesamé oil has been used.[2]

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[1] *Analyst,* 1898, 255 ; *Jahrbuch d. Chem.* 1898, 404.

[2] In case the butter has been coloured artificially, sesamé oil may have been introduced with the colouring matter, as some of the "butter colourings" are sold dissolved in sesamé oil. In that case it is necessary to shake the butter fat with hydrochloric acid until the colouring matter is removed, and then to apply the Baudouin test (Lauterwald, *Milch Zeitung,* 1902, 771).

In case it be required to state whether a butter is rancid or not, its taste gives the simplest and readiest answer. The determination of the free fatty acids in the butter fat (acid value of the butter fat) is therefore of little use, since acidity is not coterminous with rancidity. If a measure of the amount of hydrolysis which a butter fat has suffered be desired, the determination of the acetyl value—indicating in this case the amount of mono- and diglycerides—will afford the required information (cp. p. 27 and p. 271).

Since the critical temperature of dissolution (cp. p. 214) has been embodied by the Belgian Government amongst the official tests of butter fat, the following numbers may be added to those given already :—

Critical Temperatures of Dissolution (*Crismer*)

	With Alcohol, 0·7967 Specific Gravity (containing 0·9 per cent of water), at 15·5° C. in Open Tube.						With Alcohol 0·8195 (8·85 per cent of water), at 15·5° C. in Sealed Tube.	Difference.
Butter fat	*a*	*b*	*c*	*d*	*e*	*f*		
1	54·8	54·8	54·8	54·6	54·3	53·8	100·5	45·7
2	54·5	54·5	54·5	54·2	...	...	100·5	46
3	57	57	57	...	...	...	103	46
4	54	54	...	...	...	...	100·5	46
5	50	50	...	...	...	...	105·5	45·5
6	56	...	...	..	...	..	102·5	46
7	56·5	52·2	...	...	...	...	102·5	46
8	52	52·4	56·5	52·4	51·2	...	98·2	45·7
Margarine and Mixtures								
1	78	78	...	...	...	...	124	46
2	72·2	72·2	...	...	...	...	118	45·8
3	72·5	...	...	...	...	...	118	45·5
4	78	...	...	...	...	...	123·8	45·8
5	69	...	...	...	...	...	115	46·0
6	63·8	...	...	...	...	...	109	45·2
Maize oil	70·5	...	...	...	...	...	...	...

It is curious to note that in the case of a rancid butter the number of c.c. of $\frac{n}{20}$ KOH required to neutralise 2 c.c. of butter fat (dissolved in 20 c.c. of absolute alcohol), when added to the figure representing the critical temperature of the acid butter, gives approximately the critical temperature of the neutralised butter.[1]

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[1] *Bullet. de l'Assoc. Belge des Chimistes*, 1897 (10), 453 ; *Analyst*, 1897, 158.

[Table

No. of Samples.	*a* Mean Critical Temperature of Acid Butter. °C.	*b* No. of $\frac{n}{20}$ normal Alkali required for 2 c.c. c.c.	*c* Critical Temperature of Neutralised Butter. °C.	*d* Difference. *c*−*a*.
3 at 80-90° C.	88·5	7·5	96·4	7·9
14 at 90-96° C.	93·5	4·8	98·2	4·7
69 at 96-102° C.	99·12	1·2	101·7	2·6
17 at 102-106° C.	103·9	1·0		

A large number of tests based on the behaviour of butter fat with *solvents* are omitted here as entirely useless. Since, however, *Valenta's* test (cp. p. 216) is still to some extent in vogue as a preliminary test, it may be described in the form employed by *Allen*:[1] 3 c.c. of the melted fat are poured into a test-tube, an exactly equal measure of glacial acetic acid is added, and the contents of the tube heated until complete solution takes place on agitation. The liquid is then allowed to cool spontaneously whilst stirred with a thermometer, and the temperature observed at which it becomes turbid. The turbidity temperatures for genuine butter fats were found from 56°-61·5° C., whereas those for margarine were 98°-100° C.

Jean does not regard the turbidity as a criterion, but estimates the volume of acetic acid dissolved by the fat (cp. p. 218).

I subjoin some of his results in the following table:—

Fat.	Acetic Acid dissolved. Per cent.
Pure butter	63·33
,, ,, with 10 per cent of cocoanut oil .	66·66
,, ,, ,, 15 ,, ,, .	90
,, ,, ,, 28 ,, ,, .	96

With regard to a number of other methods, such as viscosimetric methods,[2] calorimetric methods,[3] cryoscopic methods,[4] and microscopical examination, the reader must be referred to the original papers.

STAG FAT

French—*Graisse de cerf*. German—*Hirschtalg*. Italian—*Sego de cervo*.

For tables of constants see p. 863.

The specimen examined by *Amthor* and *Zink*[5] had the acid value 3·5 in the fresh state, and 5·9 after keeping for one year.

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[1] *Commercial Organic Analysis*, ii. 154.

[2] Killing, *Journ. Soc. Chem. Ind.* 1895, 198; Wender, *Journ. Amer. Chem. Soc.* 1895, 719.

[3] *Journ. Soc. Chem. Ind.* 1896, 560.

[4] Garelli and Carcano, *Staz. Sperim. Agrar.* 1893. 77; Partheil, *Arch. der Pharm.* 239, 358; Peschges, *Arch. d. Pharm.*, 239, 358; Pouret, *Bulletin Soc. Chim.* 1899. iii. 21, 738.

[5] *Zeit. f. analyt. Chem.* 1897, 4.

Physical and Chemical Constants of Stag Fat

Specific Gravity.		Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.		Reichert Value.		Refractive Index. Butyro-refractometer.	
At 15° C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	At 40° C.	Observer.
0·9670	Amthor and Zink	39-40	Amthor and Zink	51-52	Amthor and Zink	199·9	Amthor and Zink	25·7	Amthor and Zink	1·66	Amthor and Zink		
		48	Beckurts[1] and Oelze	49-49·5	Beckurts and Oelze			20·5	Beckurts and Oelze			44·5	Beckurts and Oelze

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[1] *Arch. Pharm.* 1895 (233), 429.

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.		Solidifying Point.		Melting Point.		Saponification Value.		Iodine Value.	
At 15° C.	Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.
0·9685	Amthor and Zink	46-48	Amthor and Zink	50-52	Amthor and Zink	201·3	Amthor and Zink	23·6	Amthor and Zink
				49·5	Beckurts and Oelze.				

Lesser known Animal Fats

Kind of Fat.		Specific Gravity at 15 °C.		Solidifying Point.		Melting Point.		Saponification Value.		Hehner Value.	Reichert Meissl Value.	Iodine Value Per cent.		Refractive Index. Butyro-refractometer at 40°.	Observer.
	German.	Fat.	Fatty Acids.	Fat °C.	Fatty Acids °C.	Fat °C.	Fatty Acids °C.	Fat.	Fatty Acids	Per cent.	c.c. $\frac{1}{10}$ normal KOH.	Fat.	Fatty Acids.		
Domestic duck	Hausente .	...	...	22-24	...	36-39	...	...	...	...	...	58·5	...	...	Amthor and Zink[1]
Starling . .	Staar . .	...	...	15-18	30-31	30-35	38-39	209·2	...	...	...	83·7	79·4	...	,, ,,
Pigeon . . .	Taube . .	...	...	...	33-34	...	38-39	...	...	...	...	82·3	...	...	,, ,,
Turkey . .	Truthahn .	0·9220	0·9385	...	31-32	...	38-39	200·5	210·1	...	...	81·15	70·7	...	,, ,,
Bear . . .	Bär . .	0·913	...	...	...	...	...	203·4	...	...	...	80·43	...	..	Kebler and Pancoast[2]
		0·9209	...	...	...	...	32-32·05	194·8	...	...	1·66	98·5	...	53	Raikow[3]
		0·9211	...	...	...	...	30·5-31	200·4	...	...	1·15	107	...	53	,, [4]
Fox	Fuchs . .	0·9412	0·9492	24-26	36-37	35-40	41-43	191·7	205·7	...	1·30	79·7	65·4	...	Amthor and Zink
Badger . . .	Dachs . .	0·9226	0·9230	17-19	28-30	30-35	34-36	193·1	193·7	96	0·36	71·3	73	...	,, ,,
Pine marten .	Edelmarder	0·9345	...	24-27	35-37	33-40	39-43	204	...	93	1·10	70·2	53(?)	...	,, ,,
Chicken . .	Haushuhn .	0·9241	0·9283	21-27	32-34	33-40	38-40	193·5	200·8	...	1·00	66·7	64·6	...	,, ,,
Polecat . . .	Iltis . . .	...	...	...	26-27	...	34-40	...	...	...	...	62·8	60·6	...	,, ,,
Dog	Hund . .	0·9229	0·9278	21-23	34·5-35·5	37·5-40	39-40·5	195·4	199·15	95·65	0·57	58·5	50·15	...	,, ,,
Wild cat . .	Wildkatze .	0·9304	0·9366	26-27	36-37	37-38	40-41	199·9	203·8	...	2·5	57·8	58·8	...	,, ,,
Domestic cat .	Hauskatze .	0·9301	0·9251	24-26	35-36	39-40	40-41	190·7	...	96	0·90	54·5	54·8	...	,, ,,
Elk	Elch . . .	0·9625	0·9584	37-38	48-50	49-52	53-55	195·1	201·4	...	0·78	35·0	31·9	...	,, ,,
Roebuck . .	Reh . . .	0·9659	0·9622	39-41	49-50	52-54	62-64	199·0	200·5	95·8	0·99	32·1	28·9	...	,, ,,
Fallow buck .	Damhirsch .	0·9615	0·9524	40	47-48	52-53	50-53	195·6	201·4	...	1·70	26·4	28·2	...	,, ,,
Chamois . .	Gemse . .	0·9697	0·9546	42-43	51-52	54-56	57-58	203·3	206·5	...	1·80	25·0	24·4	...	,, ,,
Reindeer[5] . .	Renntier .	....	...	...	45·73	48	...	194·7	..	...	...	35·8	34·5	...	Tischtschenko[6]
,, . .	,, .	...	...	...	...	47·8	..	...	..	...	...	...	...	...	Karasseff[7]
Skunk . . .	Stinktier .	0·9166	...	...	...	...	...	206	...	...	...	...	...	...	Kebler and Pancoast[2]

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[1] *Zeit. f. analyt. Chemie*, 1897, 1.

[2] *Pharm. Journ.* 1903, 301.

[3] Body fat, *Chem. Zeit.* 1904, 274.

[4] Kidney fat.

[5] The characteristics of the milk fat from reindeer have been given above, p. 821.

[6] *Zeit. f. angew. Chemie*, 1900, 167.

[7] *Chem. Ztg.* 1899, 659. The fatty acids were stated to consist of 60·1 per cent stearic, 1·4 per cent palmitic, 38·5 per cent oleic acids.

B. WAXES

I. LIQUID WAXES

Two representatives only of this class are known hitherto, viz. sperm oil and Arctic sperm oil. As regards origin, smell, taste, and some colour reactions, they are in many respects very similar to blubber oils; so much so, that some writers class them with the latter oils. On account of their different chemical composition I have separated them from the blubber oils.

The liquid waxes contain no glycerides; they consist chiefly of compound esters of fatty acids and monovalent alcohols. They yield, therefore, on saponification large quantities of "unsaponifiable matter." This characteristic readily serves to distinguish the liquid waxes from all other fixed oils. Whereas most fatty oils yield 95 per cent of fatty acids, the liquid waxes contain only from 60 to 65 per cent of fatty acids, the remaining 40 to 35 per cent being made up by monovalent aliphatic alcohols.

The liquid waxes are further readily distinguished from the fatty oils by their low specific gravities. It is notable that their viscosity is much less influenced by variations of temperature than is the case with fatty oils.

The liquid waxes absorb very little oxygen from the atmosphere, and therefore do not dry. On treatment with nitrous acid they give a solid or butter-like elaïdin.

Some of the (fatty) blubber oils contain notable quantities of waxes, forming as it were a gradual transition from pure glycerides (seal oil) to the true liquid waxes.

SPERM OIL

French—*Huile de cachalot; Huile de spermaceti.* German—*Walratoel; Pottwaltran.* Italian—*Olio di spermaceti.*

For tables of constants see pp. 868, 869.

Sperm oil is obtained from the head cavities and from the blubber of the sperm whale, or cachelot, *Physeter macrocephalus.* On "trying" (cp. "whale oil," p. 674) the sperm whale on board ship, the head and the body blubber are kept separate, since the head oil is worth more than the body oil.[1] The oils obtained from the head matter and from the body blubber differ greatly in appearance. The former, when first taken from the head of the whale, is clear and limpid, but after a short time thickens and hardens to a white mass. The latter (the body oil) is, in its fresh state, a light straw-coloured oil.

[1] About one to two cents per gallon.

The oils are kept separate on board ship, but when received at the refineries they are generally mixed in their natural proportions and submitted together, viz. one-third head oil and two-thirds body oil, to the processes for separating the oil and spermaceti.

Sperm whales yield from 5 to 145 barrels of crude oil, averaging about twenty-five to thirty for the cows, and seventy-five to ninety for the bulls, each barrel weighing about 230 lbs.

In the refineries the crude sperm oil is allowed to stand in refrigerated chambers from ten to fourteen days at a temperature of 32° F. The partly solidified mass is then subjected to hydraulic pressure. The clear oil thus obtained is known as "winter sperm oil"; it will not congeal at 38° F., which is at present the usual commercial standard. Oils of 32° or 23° F. cold-test have also been prepared. Since the lower the temperature at which the congealed oil is pressed the less the quantity yielded, the tendency is naturally to produce oils of somewhat high cold-tests. The amount of "winter sperm oil" of 38° F. cold-tests is about 75 per cent of the crude oil. When a 32° F. cold-test was the commercial standard, the yield of "winter sperm oil" was about 67 per cent. The "winter sperm oil" is usually bleached.

After the "winter sperm oil" has been pressed out, there remains in the press-bags a solid mass of brownish colour, which is again submitted to pressure at a higher temperature (about 50° to 60° F.), whereby the oil known as "spring sperm oil" is obtained. This congeals at 50° F. to 60° F. The quantity of "spring sperm oil" is about 9 per cent of the crude oil.

The press-cakes are stored for several days at a temperature of about 80° F., and in the course of a week or so are trimmed by revolving knives, and again submitted to a high pressure in hydraulic presses. Thereby a third grade of oil, "taut-pressed oil," is obtained, which solidifies at a temperature of 90° to 95° F. The quantity of oil of this grade is about 5 per cent of the crude oil, so that from the crude sperm oil a total of 89 per cent of refined oil is obtained. The residue in the press-cloths is crude spermaceti of a brown colour. which melts at a temperature of 110° to 115° F.

Refined sperm oil is a pale yellow, thin oil, almost free from odour.

Hoffstätter's statement that sperm oil contains glycerides has been proved by *Allen* and by the writer to be erroneous. Possibly *Hoffstätter*[1] examined an oil mixed with porpoise oil, since he found in his specimen valeric acid as well as glycerol. The sperm oil fatty acids, a few characteristic constants of which are given p. 868, appear to belong to the oleic series, as shown by their iodine value, and by their property of yielding elaïdin with nitrous acid. The nature of the acids is as yet unknown. *Hoffstätter's* earlier statement that the fatty acids consist chiefly of physetoleic acid stands in need of confirmation. *Bull* isolated from two specimens of sperm oil 7·53 per cent of liquid fatty acids which had respectively the neutralisation values 183·4 and 187·9, and the iodine values 130·3 and 159·5.

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[1] *Liebig's Annalen*, 91, 177.

Lewkowitsch[1] found the acetyl values of three samples of Northern, Northern best, and Southern sperm oil, 4·49, 6·43, and 5·25 respectively.

The nature of the alcohols of sperm oil is also unknown. The writer[2] tried to resolve the mixed alcohols into their several constituents by fractional distillation of both the alcohols themselves and of their acetates, but hitherto these experiments have not led to any definite result, beyond proving that neither dodecatyl nor pentadecyl alcohol is present, and that the sperm oil alcohols belong for the most part, if not wholly, to the ethylene series, the higher members of which have been hitherto unknown.

This will be readily seen from the following table, giving the saponification values of the acetates of the five fractions into which the total amount of acetates were resolved, and the iodine values of the corresponding alcohols themselves. For the sake of comparison the theoretical numbers are given for alcohols, the presence of which might be expected.

Alcohols from Sperm Oil.	Saponific. Value of Acetate.	Iodine Value of Alcohol.
1st fraction . . .	190·2	46·48
2nd ,, . . .	183·8	63·30
3rd ,, . . .	180·7	69·80
4th ,, . . .	174·4	81·80
5th ,, . . .	161·4	84·90
Alcohol $C_{16}H_{32}O$ (unknown)	199	106·6
,, $C_{18}H_{36}O$ (unknown)	180	94·8
,, $C_{20}H_{40}O$ (unknown)	166	85·8

On heating[3] the alcohols with soda lime, they were for the most part converted into fatty acids, only 4-6 per cent of unchanged alcohol being recovered; the crude fatty acid had the acid value 181·7, and the melting point 38°-40° C.

Commercial sperm oil contains but small quantities of free fatty acids. In the following table a few numbers are recorded:—

No.	Sperm Oil.	Free Fatty Acids, as Oleic Acid. Per cent.	Observer.
1	Best quality, cold bagged .	1·46	Deering
2	Second, "hot pressed" . .	2·11	,,
3	Intermediate quality . .	0·75	,,
4	Oil of good quality . .	2·11	,,
5	Oil of doubtful quality . .	0·55	,,
6	,, ,, ,, . .	1·21	,,
7	Oil of bad quality . . .	2·06	,,
8	,, ,, ...	2·64	Thomson and Ballantyne

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[1] *Analyst*, 1899, 321.

[2] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1892, 134.

[3] *Ibid.* 1896, 41.

Physical and Chemical Constants of Sperm Oil

Specific Gravity.			Saponific. Value.		Iodine value.		Reichert Value.		Fatty Acids.		Alcohols.		Maumené Test.		Refractive Index. Oleo-refractometer.	
°C.		Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	Per cent.	Observer.	°C.	Observer.	"Degrees."	Observer.
15	0·8799-0·8835	Bull	123·4-147·4	Deering, Stoddart, Allen	84	Archbutt	1·3	Allen	60-64	Allen	39-41·5	Allen	51	Archbutt	-12 to -17·5	Jean
					81·3	Thomson and Ballantyne							45-47	Allen		
15·5	0·875-0·844	Allen									41	Lewkowitsch			-13	Archbutt and Deeley
			125·2[1]	Lewkowitsch												
,,	0·8808	Thomson and Ballantyne			86·5[3]	McIlhiney					37-41	Thomson and Ballantyne				
			127·9	,,	85·7-90·1	Bull										
			132·6[2]	,,												
99 (water at 15·5=1)	0·8303	Allen	120	Archbutt and Deeley												
			129·2-136·9	Bull												
			132·5	Thomson and Ballantyne												
													Specific. Temp. Reaction.		Butyro-refractometer.	
													100	Thomson and Ballantyne	°C. "Degrees."	Observer.
															25 54	White
															40 46·2	

Physical and Chemical Constants of the Mixed Fatty Acids

Specific Gravity.		Solidifying Point.		Melting Point.		Mean Molecular Weight.		Iodine Value.	
At 15·5	Observer.	°C.	Observer.	°C.	Observer.		Observer.	Per cent.	Observer.
0·899	Allen	16·1	Archbutt and Deeley	21·4	Archbutt and Deeley	281-294	Allen	88·1	Williams
				13·3	Williams	305	Williams	83·2-85·6	Lewkowitsch
		Titer Test.							
		11·1-11·9	Lewkowitsch						

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[1] Southern sperm oil. [2] Northern sperm oil. [3] Calculated from bromine addition value 54·54 (bromine substitution value being 1·04).

Physical and Chemical Constants of Alcohols (Unsaponifiable Matter)

Solidifying Point.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.
23-23·4	Lewkowitsch	25·5-27·5	Lewkowitsch	64·6-65·8	Lewkowitsch

Sperm oil is a valuable lubricating oil for spindles and light machinery, on account of its slight tendency to "gum," and because it retains its viscosity at higher temperatures. A sample of sperm oil examined in the writer's laboratory required in *Redwood's* viscosimeter 46·5 seconds at 70° F. (cp. also p. 207).

The comparatively high price of sperm oil suggests adulterations with fatty oils or hydrocarbon oils. The detection of these adulterants is an easy task. Admixture with Arctic sperm oil, the physical and chemical characters of which are almost identical with those of sperm oil, is, however, very difficult to detect.

The *specific gravity* of sperm oil being very low, a high density would point to the presence of fatty oils. Mineral oils of the same specific gravity cannot, of course, be detected by the determination of this constant. However, a mixture of fatty oils with hydrocarbon oils, to meet the specific gravity, would require oils of so low a specific gravity that the flash point of the resulting oil would be very low indeed.

The *low saponification value* of the oil furnishes a ready means of detecting added fatty oils, such as rape oil, blubber oils, etc. As, however, a judiciously added quantity of mineral oil may compensate the increase of the saponification value due to this cause, an oil of apparently normal saponification value may result. In fact, *Lobry de Bruyn*[1] has shown that oils occur in commerce consisting of a mixture of sperm, blubber, and mineral oils. The saponification value alone cannot, therefore, be considered as finally proving the purity of the sample.

Certainty can only be attained by examining, on the one hand, the unsaponifiable matter as detailed (p. 376) by means of acetic anhydride;[2] and, on the other hand, by estimating the amount of glycerol. The proportion of the latter multiplied by 10 will approximately yield the percentage of fatty oils.

Colour reactions are hardly required in the examination of sperm oil. Any of the liver oils, which may be used as an adulterant (*Allen*), would be detected by the sulphuric acid test in which liver oils give a violet coloration, changing to red, whereas sperm oil yields a brown colour, changing to dark brown. The readiest way to detect liver

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[1] *Journ. Soc. Chem. Ind.* 1894, 426.

[2] Absolute alcohol must not be used for the detection of mineral oil in the alcohols, as an ethyl alcoholic solution of the alcohols, even if spirit of 0·8345 specific gravity be used, is capable of holding considerable quantities of mineral oil in solution (cp. Nash, *Analyst*, 1904, 3).

oils is to determine the iodine value of the sample and the amount of glycerol obtainable on saponification.

ARCTIC SPERM OIL (BOTTLENOSE OIL)

French—*Huile de rorqual rostré.* German—*Döglingoel, Entenwalöl.*
Italian—*Olio di spermaceti artico.*

For tables of constants see pp. 871, 872.

Arctic sperm oil is obtained chiefly from the bottlenose whale, *Hyperöodon rostratus.* The principal places where this species is caught are along the edges of the ice-fields of Northern Europe, between Bear Island and Iceland. Like the sperm whale, the bottlenose whale contains a quantity of oil in the cavity of the head, which yields spermaceti. The quantity of crude oil obtainable from the bottlenose whale varies from 4 to 12 barrels, averaging about 8 barrels. The blubber oil is, as a rule, darker in colour than sperm oil; but the deodorised Arctic sperm oil of commerce so closely simulates sperm oil that it is practically impossible to distinguish the two oils by mere chemical examination. In the elaïdin test Arctic sperm oil yields a much softer elaïdin than sperm oil.

In commerce, however, these two oils are readily distinguished by their taste. Arctic sperm oil is lower in price on account of its more pronounced tendency to "gum."

Scharling, writing in the year 1848, states that Arctic sperm oil is the dodecatyl ester of doeglic acid. It hardly needs pointing out that this statement requires confirmation. In a more recent examination *Bull* obtained from two specimens of Arctic sperm oil 5·07 per cent and 3·65 per cent of fatty acids, which had the neutralisation values 154·6, 195 (?), and the iodine values 125·6, 121·2 respectively; The iodine values of these acids are lower than the iodine values of the corresponding acids obtained from sperm oil, whereas, considering the more pronounced gumming properties of Arctic sperm oil, the reverse would have been expected. *Lewkowitsch*[1] found the acetyl values of two Arctic sperm oils, 6·35 and 4·12.

The amount of free fatty acids in two samples of Arctic sperm oil examined by *Deering,* and *Thomson* and *Ballantyne,* was 2·11 and 1·97 per cent respectively. *Bull* found in two specimens 0·9 and 3·4 per cent of free fatty acids.

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[1] *Analyst,* 1899, 321.

[TABLE

Physical and Chemical Constants of Arctic Sperm Oil

Specific Gravity.		
At ° C.		Observer.
15	0·8764	Bull
15·5	0·8808	Allen
,,	0·8797	Lewkowitsch
,,	0·8799	Thomson and Ballantyne
98-99 (water 15·5=1)	0·8274	Allen

Saponification Value.	
Mgrms. KOH.	Observer.
126	Deering, Allen
123-134	Archbutt
130·4	Thomson and Ballantyne
128·4-135·9	Lewkowitsch
121·5-122·3	Bull

Iodine Value.	
Per cent.	Observer.
77·4[1]	Mills and Akitt
80·4	Archbutt
82·1	Thomson and Ballantyne
84·5	Lewkowitsch
67·1-79·7	Bull

Reichert Value.		Fatty Acids.	
c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.
1·4	Allen	61-65	Allen

Alcohols.	
Per cent.	Observer.
37·41	Allen
36·32	Thomson and Ballantyne
31·7-42·3	Lewkowitsch
34·11-34·9	,,
39·7	Archbutt and Deeley
41·1-42·6	Bull

Maumené Test.	
° C.	Observer.
42	Archbutt
41-47	Allen
Specific. Temp. Reaction.	
93	Thomson and Ballantyne

Refractive Index.	
Oleo-refractometer.	
"Degrees."	Observer.
– 13	Archbutt and Deeley

Physical and Chemical Constants of the Mixed Fatty Acids

Solidifying Point.		Melting Point.		Iodine Value.	
° C.	Observer.	° C.	Observer.	Per cent.	Observer.
10·1	Archbutt and Deeley	16·1	Archbutt and Deeley	82·2-83·3	Lewkowitsch
Titer Test.		10·3-10·8	Lewkowitsch		
8·3-8·8	Lewkowitsch				

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[1] Calculated from the bromine value.

Physical and Chemical Constants of Alcohols (Unsaponifiable Matter)

Solidifying Point.		Melting Point.		Iodine Value.	
°C.	Observer.	°C.	Observer.	Per cent.	Observer.
21·7-22·0	Lewkowitsch	23·5-26·5	Lewkowitsch	64·8-65·2	Lewkowitsch

II. SOLID WAXES

1. VEGETABLE WAXES

Vegetable waxes, the exudations of plant leaves, seem to be widely spread over the vegetable kingdom, though mostly occurring in small quantities. With the exception of carnaüba wax, flax wax, gondang wax, and pisang wax, the nature of these waxes (opium wax (p. 31), palm wax, ocuba wax, getah wax, ocotilla wax, cotton-seed wax, etc.) has been but little studied.

CARNAÜBA WAX

French—*Cire de carnauba.* German—*Carnaubawachs, Cearawachs.*
Italian—*Cera di carnauba.*

For table of constants see p. 873.

Carnaüba wax is the wax exuded by the leaves of *Corypha cerifera* (*Copernicia cerifera*), a palm indigenous to tropical South America, especially to the province of Ceara, Brazil. The wax is gathered during the months of September to March by pulling off the leaves before they have fully opened and drying them for two to three days in the sun. The white powdery mass covering the surface of the leaves is first brushed off, then scraped off, and thrown into boiling water, so that the wax collects into a solid lump on cooling.

The crude wax, as obtained from the plant, is dirty greenish, or yellowish; it is very hard, and so brittle that it can be readily powdered. The bleached wax is almost white.

Carnaüba wax dissolves completely in ether and boiling alcohol; on cooling, a crystalline mass, of the melting point 105° C., is deposited from the alcoholic solution. On ignition, commercial samples of carnaüba wax yield 0·43 per cent of ash.

Physical and Chemical Constants of Carnaüba Wax

Specific Gravity.			Solidifying Point.		Melting Point.		Acid Value.		Saponification Value.	
C.		Observer.	° C.	Observer.	° C.	Observer.		Observer.	Mgrms. KOH.	Observer.
15	0·999	Maskelyne	...	...	84·1	Mills and Akitt				
,,	0·990	Husemann-Hilger	...	...	85	Allen	4	Hübl	79	Hübl
90 (water 15·5=1)	0·8500	Allen	...	...	84	Wiesner				
			80-81	Stürcke	83-83·5	Stürcke	4-8	Allen	80-84	Allen
					85-86 [1]	,,	3·4	Henriques	78·4	Henriques [3]
98	0·8122	,,	86-87	Schaedler	90-91 [2]	Schaedler	7·0	,,	83·4	,,
							0·3-0·5	Berg	79·68	Lewkowitsch
							1·97	Lewkowitsch	80·38	,,

Physical and Chemical Constants of Carnaüba Wax—continued

Iodine Value.		Alcohols+Hydrocarbons.[4]		Fatty Acids.		Refractive Index.	
						Butyro-refractometer.	
Per cent.	Observer.	Per cent.	Observer.	Per cent.	Observer.	At 80° C. Calculated to 40° C.	Observer.
13·5	Lewkowitsch	54·87	Allen and Thomson	47·95	Lewkowitsch	65·7-69	Berg
		55	Stürcke				

[1] Recently purified. [2] Old specimen. [3] By saponification in the cold. [4] Specific gravity of the alcohols at 100° (water at 100°=1) 0·8426 (Archbutt).

Carnaüba wax consists chiefly of myricyl cerotate and small quantities of free cerotic acid and myricyl alcohol; the latter is easily removable by cold ethyl alcohol. *Stürcke*,[1] who carried out a very complete research into the chemistry of carnaüba wax, maintains that free cerotic acid is absent. The definite acid value, however, found by other observers, undoubtedly points to its presence. According to *Stürcke*, the constituents of carnaüba wax are the following:—

(1) A hydrocarbon, melting point 59°-59·5° C.
(2) An alcohol of the composition $C_{26}H_{54}O$ (ceryl alcohol), melting point 76° C.
(3) Myricyl alcohol, $C_{30}H_{62}O$, melting point 90° C.[2]
(4) A dihydric alcohol $C_{25}H_{52}O_2$ (cp. p. 131), melting point 103·5°-103·8° C.
(5) An acid $C_{24}H_{48}O_2$ (carnaübic acid), melting point 72·5° C.
(6) An hydroxy acid $C_{21}H_{42}O_3 = C_{19}H_{38}\begin{matrix}CH_2OH\\ COOH\end{matrix}$, or its lactone

Lewkowitsch[3] found the acetyl value of carnaüba wax 55·24.

Carnaüba wax is not readily saponified by alcoholic potash; this may explain the unsatisfactory agreement between the saponification numbers given in the table, p. 873.

Carnaüba wax is employed in the manufacture of candles, of polishing pastes (wax varnishes[4]), and phonograph cylinders.

Valenta[5] has examined the melting points of the following mixtures of carnaüba wax with stearic acid, ceresin, and paraffin wax:—

Proportion of Carnaüba Wax. Melting Point 85° C.	Melting Point of Mixtures of Carnaüba Wax with		
	"Stearic Acid" of Melting Point 58·5° C.	Ceresin of Melting Point 72·7° C.	Paraffin Wax of Melting Point 60·5° C.
Per cent.	°C.	°C.	°C.
5	69·75	79·10	73·90
10	73·75	80·56	79·20
15	74·55	81·60	81·10
20	75·20	82·53	81·50
25	75·80	82·95	81·70

The table shows that the addition of 5 per cent of carnaüba wax to the substances named produces a considerable increase in their melting point; further additions, however, do not cause a proportional increase.

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[1] *Liebig's Annalen*, 223, 283.

[2] Gascard (*Journ. Soc. Chem. Ind.* 1893, 955) assigns to it the formula $C_{31}H_{64}O$.

[3] *Analyst*, 1899, 321.

[4] *Journ. Soc. Chem. Ind.* 1894, 744.

[5] *Zeit. anal. Chemie*, 23, 257

Stearic acid in carnaüba wax would be detected by the high acid value of the sample; ceresin and paraffin wax by the high percentage of unsaponifiable matter.

FLAX WAX[1]

French—*Cire de lin.* German—*Flachswachs.*

The surface of the flax fibre is coated with a waxy substance which can be isolated by extraction with volatile solvents.

The flax wax so obtained is a white or yellowish-green or yellowish-brown solid substance of dull, wax-like fracture and possessing a very pronounced odour of flax. The wax dissolves with difficulty in chloroform, but is readily soluble in the usual solvents. In alcohol it is only partially soluble.

The fatty acids in the flax wax[2] consist of the saturated acids: palmitic and stearic, and of the liquid acids: oleic, linolic, and linolenic. The identity of the liquid acids was proved by the isolation of their oxidation products. The 81·3 per cent of alcohols *plus* hydrocarbons given in the table consist in the main (to the extent of 70-80 per cent) of a solid hydrocarbon, melting at 68° C., and having the specific gravity 0·9941 at 10° C. The remainder is a mixture of phytosterol and ceryl alcohol.

Physical and Chemical Constants of Flax Wax[2]

Specific Gravity at 15° C.	Melting Point. ° C.	Acid Value.	Saponification Value. Mgrms. KOH.	Iodine Value. Per cent.	Reichert-Meissl Value. cc. $\frac{1}{10}$ norm. KOH.	Alcohols + Hydrocarbons. Per cent.
0·9083	61·5	54·49	101·51	9·61	9·27	81·32

GONDANG WAX[3]

This wax is obtained by the Javanese from the latex of a wild fig-tree, gondang (*Ficus ceriflua*, Jungh; *Ficus subracemosa*, Bl.), by boiling the latex with water until the wax separates. The cakes of gondang wax are hard; they have a chocolate colour at the outside, and are yellowish-white on the inside. The yellowish-white colour becomes gradually brown on exposure to the air. The wax shows conchoïdal fracture, but is not very friable. The crude wax is stated to form a transition product between india-rubber and wax. The crude wax melts at about 60° C.; it then forms an extremely viscous mass which can be drawn out in threads, and separates on standing

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[1] Cross and Bevan, *Journ. Chem. Soc.* 1890, 196.

[2] C. Hoffmeister, *Berichte*, 1903, 639.

[3] Greshoff and Sack, *Rec. des Trav. Chim. des Pays-Bas*, 1901, 65.

into two layers—melted wax and a brown aqueous layer. On cooling, the wax remains viscous for some time; a white mass finally separates.

The specific gravity of the melted wax is 1·0115 at 15° C.; it softens at 55° C., but is not completely melted at 73° C. It dissolves in benzene, carbon bisulphide, chloroform, oil of turpentine, petroleum ether, as also in boiling ether, alcohol, and amyl alcohol. By purifying it with boiling alcohol 70 per cent are obtained of a white crystalline mass, having the melting point 61° C., soluble in boiling alcohol and insoluble in cold alcohol.

The purified wax of the melting point 61° C. consists chiefly of the ficoceryl ficocerylate.

On subjecting gondang wax to destructive distillation, an aqueous distillate containing acetic acid and propionic acid is obtained first, followed by an oily liquid containing a hydrocarbon, $C_{14}H_{26}$, a crystalline acid, melting at 54° C., of the formula $C_{12}H_{24}O_2$, and an alcohol of the formula $C_{44}H_{88}O$, melting at 51° C.

PISANG WAX[1]

Pisang wax is found as a powdery mass on the leaves of *Cera Musæ*, indigenous in Java. The natives collect the wax in much the same manner as carnaüba wax is gathered, by scraping it off from the leaves and melting the scrapings in boiling water. One branch carrying about seven leaves, each about 6 feet long on an average, yields 60 grams of wax. The exported wax forms hard cakes of white, yellowish, or slightly green colour. The wax is slightly transparent, of granular crystalline fracture, and easily friable. The commercial product contains only 1 per cent of ash.

The specific gravity varies from 0·963 to 0·970, the melting point is from 78°-81° C.

The wax dissolves sparingly in strong boiling alcohol; it is also sparingly soluble in most solvents. It dissolves easily, however, in boiling oil of turpentine, amyl alcohol, and carbon bisulphide. At 15° C. the following quantities are retained in solution: by petroleum ether 0·1 per cent, acetone 0·5 per cent, ether 0·7 per cent, oil of turpentine 1 per cent, chloroform 1·7 per cent, and carbon bisulphide 1·8 per cent.

The wax is the pisangceryl ester of pisangcerylic acid. The commercial samples contain only 1 to 1·5 per cent of free fatty acids.

On subjecting the wax to destructive distillation a small quantity of aqueous distillate is obtained, passing over whilst the thermometer rises rapidly to 200° C. At 210°-320° C. a buttery mass distils over, which can be separated by expression into a liquid and a solid portion. The liquid portion purified by sulphuric acid and redistillation appears to be a hydrocarbon having the formula $C_{16}H_{34}$. The solid mass melts after being crystallised from alcohol at 63·5° C., and is stated to have the composition expressed by the formula $C_{27}H_{54}O_2$.

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[1] Greshoff and Sack, *Rec. des Trav. Chim. des Pays-Bas*, 1901, 65.

PALM WAX

This wax is obtained from *Ceroxylon andicola* (indigenous to the Andes) and *Klopstockia cerifera* (indigenous to Columbia). These two palms exude from their trunks a wax-like mass which is collected by the natives. It is a greenish-white powder; it is purified in a somewhat crude fashion by melting over fire and boiling with water. This crude product is stated to be a mixture of pure wax with a resinous substance, which can be removed by repeated crystallisation from boiling alcohol, in which the resinous matter is readily soluble. The chemical characteristics are stated to be very similar to those of carnaüba wax. It should, however, be noted that commercial products sold as palm wax have frequently been found to be nothing else but carnaüba wax.

Lesser known vegetable waxes are getah wax (from the wax fig-tree, *Ficus ceriflua ?*); the wax from *Ficus rubiginosa* (*Warren de la Rue* and *Müller*), the wax from *Antiaris toxicaria*, ocotilla wax, cotton-seed wax, and Madagascar Rhimba wax.

2. ANIMAL WAXES

The animal waxes contain but small quantities of unsaturated acids and unsaturated alcohols. The acid and alcoholic constituents of beeswax, spermaceti, and insect wax belong chiefly to the saturated (aliphatic) series. Wool wax, however, has an exceptional chemical composition; some of its alcohols are derivatives of the aromatic series, and its fatty acids are characterised by the facility with which they become dehydrated. Wool wax is also remarkable for the great difficulty with which it is saponified even by alcoholic caustic potash.

WOOL WAX[1] (WOOL GREASE)

The term *wool wax* has been proposed by the writer for the neutral portion of the raw wool fat—wool grease.

WOOL FAT, WOOL GREASE, RECOVERED GREASE, BROWN GREASE[2]

French—*Suint*. German—*Wollfett*, *Wollschweissfett*.
Italian—*Grasso di lana*.

For tables of constants see pp. 880, 881.

Wool fat is the natural grease contained in sheep's wool. In the course of preparing the raw wool for spinning this grease is removed

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[1] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1892, 135; 1896, 14.

[2] In the United States this grease is known commercially as "Dégras."

by means of dilute soap (or sodium carbonate) solutions, or by extraction with volatile solvents. In this country the suds from wool-scouring are usually collected in large tanks, and by acidulating with mineral acids, "brown grease," or "recovered grease,"[1] is obtained of varying composition, according as the suds from the wool are kept separate or are mixed with the soap suds from the scoured woven goods, as is the case in those woollen mills where wool is washed, spun, and woven (cp. chap. xvi. "Waste Fats").

The wool grease, obtained by extracting raw wool with volatile solvents, contains, of course, only the natural constituents, viz. free fatty acids, neutral esters, and free alcohols, in admixture with potassium salts of fatty acids.

The wool fats from various sources vary considerably within certain limits, much as other natural products do. The following table contains some characteristics of several wool fats obtained by extracting raw wool with ether:—

Source of Wool Fat. From	Yield of Wool Fat. Per cent.	Potash Salts in Wool Fat calculated to Potassium Oleate. Per cent.	Colour.	Consistence.	Acid Value.	Saponification Value.	Alcohols (unsaponifiable). Per cent.	Observer.
1. New Zealand wool	16·6	4·9	dark red	fairly soft when fresh, becomes harder on keeping.	14·3	110·5-110·7	43·6-43·9	Herb
2. Australian wool	16·0	4·24	brownish-yellow	fairly soft, remained so after keeping.	15·5	112·7-113·3	..	..
3. South American wool	13·2	9·25	yellowish-olive-green	fairly hard.	13·2	98·7-98·9	43·1-43·6	..
4. Russian wool	6·6	24·4	dirty brown	soft at 20° C.	13·9	94·2-95·9	38·7-39·1	..
5. ?			light brown	melts at 30·6	27·4	100·8	55·12	Lewk-witsch

Since the valuable property of wool fat, viz. that of yielding with water emulsions which are easily absorbed by the skin, has been rediscovered,[2] the raw wool fat is purified by various (patented[3]) processes, and the thus purified neutral wool fat is brought into commerce either in an anhydrous state (under such names as "adeps lanæ"), or in the hydrated state (under the name "lanolin"). Other commercial names are "agnin," "alapurin," etc.

Anhydrous wool wax is a pale yellow, translucent substance, having a slight but not unpleasant smell (in contradistinction to raw wool grease, which is characterised by its peculiar disagreeable smell, recalling that of sheep). Its consistence is that of a thin ointment.

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[1] In the United States this grease is known commercially as "Dégras."

[2] *Journ. Soc. Chem. Ind.* 1892, 136; 1896, 14.

[3] Cp. Langbeck, *Journ. Soc. Chem. Ind.* 1890, 356.

It dissolves readily in chloroform, ether, and ethyl acetate. Although insoluble in water, it possesses the remarkable property of absorbing larger quantities of water than any other wax. The emulsion it forms with water has the appearance of a perfectly homogeneous mass. Thus wool wax can be mixed with as much as 80 per cent of water. A mixture of neutral wax and water, containing about 22-25 per cent of the latter, is sold in commerce under the name "lanolin" (see below).

Wool wax is not completely saponified by aqueous caustic alkalis; even prolonged boiling with alcoholic potash under ordinary pressure does not effect complete saponification. Sodium alcoholate (or absolute alcohol and metallic sodium) or alcoholic potash under pressure readily effect complete saponification (cp. chap. ii. p. 60).

The chemical composition of wool wax is not fully known. For table of constants see p. 880. Wool wax evidently consists of a very complex mixture of esters and free alcohols; amongst the alcohols, cholesterol and isocholesterol occur to a large extent. *Lewkowitsch* was the first to show that the previously accepted statement, viz. that neutral wool wax is a mixture of cholesteryl (and isocholesteryl), oleates, and stearates, is erroneous. The low iodine value of both the fatty acids and the alcohols precludes this altogether. The absence of palmitic and stearic acids has been confirmed later on by *Darmstädter* and *Lifschütz*.[1] Nor is the presence of ceryl cerotate,[2] asserted by *Buisine*, to be accepted without further proof, as ceryl alcohol occurs in raw wool fat in the free state. An inquiry into the nature of the components carried out by the writer,[3] has shown that the mean molecular weight of the alcohols (239), in conjunction with the low iodine value (36), points to the presence of lower saturated alcohols, since cholesterol and isocholesterol have the molec. weight 372, and the iodine absorption 68·3 (cp. chap. ii. p. 139). The fatty acids, owing to their low iodine absorption, cannot consist to any considerable extent of oleic acid. I have shown that they contain hydroxy acids,[3] as they easily give off the elements of water at temperatures little above 100° C., with formation of inner anhydrides or lactones, and assimilate considerable quantities of acetic anhydride, forming acetylated acids.

Marchetti[4] stated that he isolated from wool wax an alcohol of the formula $C_{12}H_{24}O$—termed lanolin alcohol. Since, however, two other alcohols described by *Darmstädter* and *Lifschütz*,[5] and supposed to form a homologous series with lanolin alcohol, have been shown to be lactones (see above), the existence of this alcohol becomes doubtful.

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[1] *Berichte*, 1898, 103.

[2] G. de Sanctis, *Chem. Zeit.* 1895, 651, states that cerotic acid occurs in wool fat. According to *Darmstädter* and *Lifschütz*, the quantity of cerotic acid can only be very small.

[3] *Journ. Soc. Chem. Ind.* 1892, 136 ; 1896, 14.

[4] *Gazz. Chimica*, 1895, 22.

[5] *Berichte*, 1895, 3133, cp. *Jahrbuch der Chemie*, vi. 375.

I. *Physical and Chemical Constants of Wool Wax* (i.e. *Esters and Free Alcohols*)

Specific Gravity.			Solidifying Point.		Melting Point.		Saponific. Value.		Iodine Value.		Fatty Acids.		Alcohols.	
°C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	Per cent.	Observer.	Per cent.	Observer.
17	0·9449[3]	Rosauer	30-30·2[1]	Lewkowitsch	39-42·5	Stöckhardt	98·3	Allen	25·9-26·8[1]	Lewkowitsch	59·8	Lewkowitsch	43·6	Lewkowitsch
17	0·9413[4]	,,			36-41	Benedikt	102·4[1]	Lewkowitsch	25·8-28·9[1]	,,			51·8[2]	,,
98·5 (water 15·5=1)	0·9017	Allen							17·1-17·6[2]	,,				
					31-35 39-41 [1]	Lewkowitsch								

II. *Physical and Chemical Constants of the Mixed Fatty Acids*

Solidifying Point.	Melting Point.	Mean Molecular Weight.	Iodine Value.	Observer.
°C. 40	°C. 41·8	327·5	Per Cent. 17	Lewkowitsch.

[1] From raw wool fat.
[2] Prepared from "lanolin."
[3] From anhydrous lanolin.
[4] From "Adeps lanæ," *Chem. Centr.* 1898, ii. 875.

III. *Physical and Chemical Constants of the Mixed Alcohols*

Solidifying Point. °C.	Melting Point. °C.	Mean Molecular Weight.	Iodine Value.	Acetyl Value.	Observer.
28[1]	33·5[1]	239[1]	36[1]		Lewkowitsch
			26·4[2]	143·8[2]	,,

IV. *Chemical Constants of the Neutral Esters*

Saponification Value.		Fatty Acids.		Alcohols.	
Mgrms. KOH.	Observer.	Per cent.	Observer.	Per cent	Observer.
96·9	Lewkowitsch	56·66	Lewkowitsch	47·55	Lewkowitsch

The results of a further examination of wool wax carried out by *Darmstädter* and *Lifschütz*[3] have been collated by me in a synoptical form in the following table:[4]—

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[1] From raw wool fat. [2] From lanolin.

[3] *Berichte*, 1896, 618; 2890; *Journ. Soc. Chem. Ind.* 1896, 548; 1897, 150.

[4] *Jahrbuch der Chemie*, viii. 405.

[Table

Wool wax[1] *separated by Amyl Alcohol into two Parts: A. and B.*

A. Hard Portion,[1] forming about 10 to 15 per cent Wool Wax. Resolved into		B. Soft Portion, forming about 85 to 90 per cent of Wool Wax. Resolved into			
(α) Acids, about 60 per cent.	(β) Alcohols, containing	(α) Acids about 40 to 50 per cent, containing	(β) Alcohols; about 55 to 60 per cent resolved by means of Methyl Alcohol into two Fractions.		
			1st Fraction resolved into Two Groups.		2nd Fraction, containing
			1st Group.	2nd Group.	
(1) Lanoceric acid (2) Lanopalmic acid (3) Myristic acid (4) Carnaübic acid (5) A liquid acid (6) A volatile acid	(1) Ceryl alcohol (2) Carnaübyl alcohol (3) Cholesterol *Isocholesterol* is absent	(1) A liquid acid (about 40 per cent) (2) Myristic acid (3) Carnaübic acid Neither lanoceric nor lanopalmic acids were present	Containing ceryl alcohol, carnaübyl alcohol	Containing small amounts of ceryl and carnaübyl alcohols, and chiefly isocholesterol (11 per cent) differing from *Schulze's* isocholesterol as regards crystalline form, solubility, and composition, but identical with it as regards melting point and chemical reactions	Alcohol 2 *a* (3-4 per cent of B) Alcohol 2 *b* (6-7 per cent of B) Alcohol 2 *c* (50-54 per cent of B)

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[1] *Darmstädter* and *Lifschütz* term the hard fat A. "Wool wax," but for chemical reasons the name wool wax should embrace all the neutral portions contained in wool fat.

The alcohols mentioned under B (β) do not contain cholesterol. The alcohol "2 *c*" gives the colour reactions of cholesterol, but since cholesterol itself could not be isolated, *Darmstädter* and *Lifschütz* concluded that cholesterol is only formed during the reaction, and that the alcohol "2 *c*" should be looked upon as a hydrated cholesterol, from which cholesterol and isocholesterol are obtained. Further researches are required to elucidate the complicated composition of wool wax. Since cholesterol and isocholesterol differ in their optical rotation (cholesterol being lævorotatory and isocholesterol being dextro-rotatory in ethereal solution), the polariscopic examination of the alcohols should lead to more definite information. This is all the more required since in a recent publication (*Berichte*, 1898, 1200) *Schulze* maintains his earlier statements on isocholesterol.

To some extent the difference in the results obtained by the several observers may be due to the difference in the composition of the wool fats from which the wool waxes were isolated.

Lewkowitsch[1] found the acetyl value of a sample of wool wax from "lanolin" 23·3, and of the wool fat alcohols 143·8.

Owing to its property of forming an emulsion with water (which will not separate into two layers even after several years' standing), and to the ease with which it is absorbed by the skin, wool wax is used as a basis for ointments and cosmetics. The British Pharmacopœia recognises two preparations, viz. Adeps lanæ, *i.e.* pure wool wax, and Adeps lanæ hydrosus, *i.e.* hydrous wool wax, better known under the trade term "Lanolin."

BEESWAX[2]

French—*Cire des abeilles.* German—*Bienenwachs.* Italian—*Cera d' ape.*

For table of constants see p. 887.

Beeswax is secreted by the common bee (*Apis mellifera*) as a product of digestion; it serves to the bees as the material for building up the honeycombs.[3]

The older processes of preparing beeswax consisted in melting the honeycombs by immersion into hot water, and filtering the liquefied wax from impurities (such as dead bees, etc.) A more modern process is to prepare the wax by expression after having melted the honeycombs and strained from gross impurities. The press residue is again boiled up and pressed once more. The residue from the second expression still contains some 10 to 15 per cent of

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[1] *Analyst*, 1899, 321.

[2] The bibliography of beeswax arranged chronologically, and of waxes used in adulterating it, will be found *Journ. Soc. Chem. Ind.* 1892, 756.

[3] The propolis (German—"Klebwachs"), *i.e.* the wax used by the bees for sealing up the cells, consists, according to Greshoff and Sack (*Rec. Trav. Chim. des Pays-Bas*, 1903, 139), of 84 per cent of an aromatic resin, 12 per cent of wax, and 4 per cent of alcohol-soluble impurities.

wax. Such residues are collected together by special establishments, and the wax is recovered by extraction with solvents. This wax, known as "extracted beeswax," differs somewhat from the beeswax obtained by expression. It represents a dark brown soft mass, greasy to the touch and of unpleasant odour; on boiling with water it yields a yellow colouring matter to the water. *Hirschel*[1] examined three genuine samples of "extracted" wax. Chemically they differ from the expressed wax by a somewhat higher acid value (23·3 to 27·1) and a much higher iodine value (31·2-39·6). In *Weinwurm's* paraffin wax-, or ceresin-test (see p. 900), they behave like samples of genuine beeswax containing about 5 per cent of admixed paraffin wax. Since "extracted" beeswax is hardly sold in commerce as such, the following notes refer only to expressed wax, *i.e.* the yellow wax of commerce.

The expressed wax is, as a rule, of a yellow or yellowish colour. Some commercial waxes, mostly of non-European origin, have a greenish, reddish, or brown colour. Yellow wax has the pleasant odour of honey, and is almost tasteless. At low temperatures it is brittle, and of fine granular fracture. By repeated melting in water, or by exposure to sunlight, in the shape of granules, or strips, or ribbons, *white wax* is obtained.[2] This is of a pure white or slightly yellowish colour, odourless and tasteless. It has a higher specific gravity than yellow wax, and is more brittle than the latter. It is transparent at the edges; its fracture is smooth, and no longer granular.

In practice it is customary to mix with the yellow wax previous to air-bleaching 3 to 5 per cent of tallow, or a small quantity of oil of turpentine, so as to accelerate the process. These additions at the same time prevent the wax from becoming too brittle. Yellow wax is also decolorised by treatment with animal char or with chemicals, such as potassium permanganate, potassium bichromate, and sulphuric acid, and hydrogen peroxide (cp. table, p. 895).

Beeswax is not greasy to the touch, but if dropped on paper in the melted state it causes a permanent transparent spot.

A normal constituent of wax is pollen, so that wax which has only been strained may be detected by microscopic examination.

Beeswax[3] consists chiefly of a mixture of crude *cerotic acid*[4] (cp. p. 97) and *myricin* (myricyl palmitate). It also contains, in small quantities, free melissic acid, $C_{30}H_{60}O_2$, or $C_{31}H_{62}O_2$, *myricyl alcohol* (*Schwalb*),[5] uncombined *ceryl alcohol*, and another alcohol of unknown composition. Small quantities of unsaturated fatty acids have also

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[1] *Chem. Zeit.* 1904, 212.

[2] Cp. also Rambo, *Journ. Soc. Chem. Ind.* 1897, 150.

[3] Brodie, *Liebig's Annalen*, 67. 180; 71. 144. Schalfejeff, *Berichte*, 9. 278; 1688. Nafzger, *Liebig's Annalen*, 224. 225; Schwalb, *ibid.* 235. 106. Marie, *Journ. Soc. Chem. Ind.* 1894, 207; 1895, 599; 1896, 362.

[4] Containing about 30-40 per cent of homologous acids (Marie). The melting point of the isolated and recrystallised "cerotic" acid is given by various observers as 78°-79° C.

[5] According to Gascard (*Journ. Soc. Chem. Ind.* 1893, 955), the myricyl alcohol from beeswax is identical with that from carnaüba wax and has the formula $C_{31}H_{64}O$.

been found. Hydrocarbons also are normal constituents of beeswax. *Schwalb* has isolated two hydrocarbons:—*heptacosane*, $C_{27}H_{56}$, melting point 60·5° C., and *hentriacontane*, $C_{31}H_{64}$, melting point 67° C. (cp. below, p. 901).

The ratio of free (cerotic) acid to myricin has been found by *Hehner* and *Hübl* in a number of well-agreeing experiments as 14 : 86 (see below).

With regard to the proportion of hydrocarbons in beeswax the earlier statement made by *Schwalb*, who found 5-6 per cent, is erroneous; for *A.* and *P. Buisine* obtained from 12·7 to 13·0 per cent of hydrocarbons. These belong partly to the ethylene series. *Mangold*[1] confirmed *Buisine's* results. *Kebler* found 12·5-14·5 per cent. More recently *Heit* and *Ahrens* obtained from 12·8 to 17·35 per cent of hydrocarbons (cp. p. 902).

Beeswax is almost insoluble in cold alcohol. Boiling alcohol dissolves the bulk of the cerotic acid and a small quantity of myricin. The alcoholic solution reddens blue litmus paper faintly; a solution of phenolphthalein made just pink by a trace of alkali, is however instantly decolorised. On cooling, the cerotic acid separates out so completely (in the form of thin needles) that the alcoholic solution does not become turbid on mixing with water, a slight opalescence only being noticeable. Warm ether dissolves beeswax readily; on cooling, however, a portion of the dissolved wax separates out.

The free cerotic acid cannot be extracted by treatment with sodium carbonate or caustic alkali, the resulting soap solution forming with the beeswax esters a complete emulsion which does not separate even after many months' standing (similarly as in the case of wool wax).

On distilling beeswax with lime, an oil is obtained—beeswax oil.[2] *Greshoff* and *Sack*[3] obtained, on subjecting beeswax to destructive distillation, an oily distillate which separated into a solid and a liquid portion. The liquid portion contained a hydrocarbon of the composition $C_{15}H_{30}$. The solid portion still contained undecomposed wax, and gave after saponification a solid fatty acid of the melting point 63° C. The unsaponifiable matter contained a hydrocarbon of the composition C_nH_{2n} melting at 56° C.

Beeswax is very frequently adulterated. *Water* and *mineral matters* (such as ochre, gypsum, etc.), also *flour* and *starch*, are easily detected. Fraudulent admixture with *tallow*, *Japan wax*, *stearic acid*, *paraffin wax* and *ceresin*, *colophony*, *wool wax*, *carnaüba wax*, *insect wax* may be detected by the methods described below.

Preliminary Tests

Long[4] recommends to dissolve the sample in chloroform, and to examine a few drops microscopically on an object glass. When the

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[1] *Journ. Soc. Chem. Ind.* 1891, 861.

[2] *Liebig's Annalen*, 2. (1832) 255; *Journ. Soc. Chem. Ind.* 1895, 1050.

[3] *Rec. Trav. Chim. des Pays-Bas*, 1901, 75.

[4] *Chem. Zeit.* 9. 1504.

solvent has evaporated so far that a solid particle is seen, the cover is placed on the wax and the crystals examined. In the case of pure wax characteristic tufts of crystals are noticed, having the shape of dumb-bells, the spheres of which consist of curved needles. In presence of about 20 per cent of paraffin wax, tallow, or stearic acid, the microscopic appearance is changed completely; paraffin wax apparently preventing the formation of crystals, whereas in the presence of fats and fatty acids the crystals characteristic of the latter are noticeable.

Since pure beeswax is soluble in chloroform, whereas ceresin, paraffin wax, carnaüba wax, and wool wax are not completely soluble in this menstruum, considerable quantities of the latter may thus be detected approximately. It should, however, be borne in mind, that bleached (white) beeswax is not readily soluble in chloroform (*Dieterich*).[1]

Previous to the further examination by physical and chemical tests, the sample of beeswax should be boiled with water (to remove honey) and filtered in a water oven. Gross adulterants, such as mineral matters, are thus easily detected and determined quantitatively. The determination of *water* should not be omitted.

As a preliminary test to which the filtered wax may be submitted, refractometric examination has been recommended by *Prosio*, *Marpmann*, *Werder*,[2] and later by *Berg*.[3] Owing to the high melting point of the wax, the refraction should be determined at 75°-80° C. Since the melting point of most beeswaxes lies above 65° C., the numbers recorded in the literature on this subject for a temperature of 62° C. have been omitted, as being open to serious doubts. The figures given in the table have been determined at 84° C., but were reduced by calculation to 40° C. (*Berg*). (The actually observed numbers have not been published.) Considerable quantities of carnaüba wax, colophony, ceresin, paraffin wax, and stearic acid, can be preliminarily detected by the refractometric method, as will be seen from the following numbers:—

	Butyro-refractometer. Scale divisions at 84° C., calculated to 40° C.
Commercial stearic acid	29·8-33·3
Japan wax	47·6-49·7
Carnaüba wax	65·7-69
Beeswax	42·9-45·6

As a further preliminary test the *specific gravity* of the sample should be taken. The numbers recorded in the table (p. 887) will afford the necessary guidance. Of course, the specific gravity[4] test alone does not give a final answer as to purity, since the artificial compounds (see below) can easily be prepared so as to exhibit the specific gravity of a genuine beeswax.

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[1] *Chem. Zeit.* 1898, 730; *ibid.* 1903, 808.

[2] *Ibid.* 1898, 58.

[3] *Ibid.* 1903, 752.

[4] Mastbaum (*Zeit. anal. Chem.* 1902, 929) recommends a special contrivance for the determination of the specific gravity.

Physical and Chemical Constants of Beeswax

Specific Gravity.			Solidifying Point.		Melting Point.		Acid Value.		Saponification Value.	
°C.		Observer.	°C.	Observer.	°C.	Observer.		Observer.	Mgrms. KOH.	Observer.
15	0·965-0·975	Hager	60·5[1]	Allen	63[1]	Allen	20	Hübl	95	Hübl
,,	0·962-0·966[1]	Dieterich	62[5]	,,	63·5[5]	,,	18·6[2]	Dieterich	90·4-91·4[2]	Dicterich
,,	0·964-0·968[2]	,,	61·5[6]	,,	63·0[6]	,,	16·8-20·6[1]	,,	87·8-96·2[1]	,,
,,	0·959-0·966[3]	Camilla	60·5-62·8[3]	Camilla	65[2]	Barfoed	19·02-20·6[1]	Buisine	97-107	Becker
,,	0·959[4]	,,	61·9-63·4[8]	Mastbaum	69-70[2]	Lepage	19·04-20·9[3]	Camilla	93·5-97·1[1]	Lewkowitsch
,,	0·964-0·970	Hett and Ahrens			63-64·4[3]	Camilla	20·9-21·2[4]	,,	90·1-98·89[1]	Hett and Ahrens
					62·5-63·6[4]	,,	20·6-21·09[1]	Lewkowitsch		
80 (water 15·5=1)	0·8356[1]	Allen					18·37-20·94[1]	Hett and Ahrens		
98	0·8221[1]	,,								
98-99	0·827[5]	,,								
,,	0·818	,,								

Physical and Chemical Constants of Beeswax—continued

Iodine Value.		Reichert-Meissl Value.		Alcohols+Hydrocarbons[9] (Unsaponifiable).		Refractive Index. Butyro-refractometer.		Fatty Acids.	
Per cent.	Observer.	c.c. $\frac{1}{10}$ norm. KOH.	Observer.	Per cent.	Observer.	"Degrees."	Observer.	Per cent.	Observer.
8·3-11	Buisine	0·34-0·41[3]	Camilla	55·25	Schwalb	42·9-45·6 determined at 84° C. calcul. to 40° C.	Berg	46·77	Lewkowitsch
7·9-8·9	Guyer[7]	0·54[4]	,,	52·38	Allen and Thomson				
				55·58[1]	Lewkowitsch				

[1] Yellow wax. [2] White wax. [3] Italian waxes not Ligurian. [4] Ligurian wax from *Apis Ligustica Spinola.* [5] Chemically bleached. [6] Air bleached. [7] Eleven samples of pure English waxes (*Journ. Pharm.* 1897, 308). [8] 17 Portuguese waxes. [9] Specific gravity at 100° (water at 100°=1)=0·8239 (Archbutt).

The *melting point* of the sample should also be taken, although this test either alone or in conjunction with the specific gravity, does not afford decisive information, inasmuch as mixtures having the specific gravity as also the melting point of genuine beeswax can be readily prepared.

The most important test for the detection of adulteration is the determination of the *acid value* and of the *saponification value.*

The determination of the *acid value* is carried out in the usual manner (described in Chap. VI. p. 277), by warming 3 to 4 grms. of the sample with 20 c.c. of 96 per cent alcohol in a flask until the wax is melted, distributing the wax by shaking, and titrating with standardised (about half-normal) alcoholic potash, phenolphthalein being the indicator. Care must be taken that the wax remains in a melted state during the operation. If the solution is diluted with a large quantity of alcohol and kept hot, the acid value may also be determined with aqueous half-normal alkali.

The determination of the *saponification value* should be carried out on a separate quantity of wax, as unless strongest alcohol has been used in the determination of the acid value, the saponification of the wax may not be easily completed. It has been pointed out already that waxes are not saponified with the same facility as are oils and fats. The difficulties encountered by a number of analysts in saponifying beeswax has led to a number of proposed modifications, which are altogether unnecessary if the saponification be carried out with strongest alcohol. The wax should be saponified with alcoholic potash prepared with at least 96 per cent of alcohol. Even then the saponification cannot be considered as complete after half an hour, as experiments instituted in my laboratory showed that after that time saponification values of only 60 were obtained, whereas if the wax was boiled with alcoholic potash over free fire for at least an hour complete saponification was effected.[1] More readily still is complete saponification effected by employing sodium alcoholate (Chap. II. p. 60).

Henriques' process of cold saponification cannot be recommended. The employment of caustic soda causes difficulties, the soda soaps of beeswax fatty acids being less readily soluble than the potassium salts. Indeed, *Henriques* later on modified his method by proposing to use petroleum ether of a boiling point of not less than 120° C., and to boil the solution of wax in such petroleum ether with alcoholic caustic soda. The necessity of operating with a boiling solution entirely disposes of the possibility of saponifying "in the cold."

In pure beeswax the amount of free acid stands in a definite proportion to the amount present in the form of combined esters. This was pointed out first by *Hehner*,[2] who calculated the amount of alkali

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[1] It is unnecessary to boil 4-8 hours, as recommended by *Berg*. In order to carry out the saponification at a higher temperature Eichhorn (*Zeit. anal. Chem.* 1900, 39, 640) employs amyl alcohol as a solvent.

[2] *Analyst*, 1883, 16.

used for determining the free fatty acids to "cerotic" acid, on the assumption that 1 c.c. of normal KOH neutralises 0·410 grms. of free acid, and the alkali used for the saponification of the neutral esters—*i.e.* the difference between the saponification value and the acid value—to "myricin." Thus 1 c.c. of normal KOH was taken to saponify 0·676 grm. of myricin.

In the following table a number of *Hehner's* analyses are collated :—

Kind of Wax.	Cerotic Acid.	Myricin.	Total.
	Per cent.	Per cent.	Per cent.
Wax from Hertfordshire	14·35	88·55	102·90
,, ,,	14·86	85·95	100·81
,, Surrey	13·22	86·02	99·24
,, Lincolnshire	13·56	88·16	101·72
,, Buckinghamshire	14·64	87·10	101·74
,, Hertfordshire	15·02	88·83	103·85
,, New Forest	14·92	89·87	104·79
,, Lincolnshire	15·49	92·08	107·57
,, Buckinghamshire	15·71	89·02	104·73
Wax from America	15·16	88·09	103·25
,, Madagascar	13·56	88·11	101·67
,, Mauritius	13·04	88·28	101·32
,, ,,	12·17	95·68	107·85
,, ,,	13·72	96·02	109·74
,, Jamaica	13·49	85·12	98·61
,, ,,	14·30	85·78	100·08
,, Mogadore	13·44	89·00	102·44
,, Melbourne	13·92	89·24	103·16
,, ,,	13·18	87·47	100·65
,, Sydney	13·06	92·79	105·85
,, ,,	13·16	88·62	101·78

Hübl,[1] working on beeswax about the same time as *Hehner*, expressed the results of the examination of beeswax by simply stating the acid value and the saponification value in terms of Mgrms. KOH (cp. Chap. VI. p. 226). The acid values of a number of samples of yellow wax were found by *Hübl* from 19 to 21, mostly 20; and the saponification value from 92 to 97, mostly 95. Since in *Hübl's* opinion the higher and lower values occur together as a rule, he assumed that the amount of free fatty acids stood in a definite—almost constant—ratio to the amount of esters. He therefore brought the amount of alkali required for neutralising the free acid—*i.e.* the acid value—in numerical relation to the amount of alkali required to saponify the neutral esters. The difference between the saponification and the acid value was termed by him "ether value." (For reasons stated above, p. 280, the term "ether value" or "ester value" has been abandoned in this work.) This ratio is 20 : 75 = 3·75 (75 being the difference between the saponification value, 95, and the acid value, 20). *Hübl* found in a number of beeswaxes that this "ratio number" varied between 3·6 and 3·8, and he therefore

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[1] *Dingl. Polyt. Jour.* 249 (1883), 338.

assumed that a beeswax, the "ratio number" of which deviated much from 3·7, must be adulterated.

From *Hehner's* numbers given above the "ratio number" 3·9 can be calculated; this is in satisfactory agreement with *Hübl's* ratio number 3·75.

In order to emphasise the importance of the "ratio number" for the detection of adulteration, I collate in the following table the "ratio numbers" of some substances that are likely to be used in the adulteration of beeswax:—

Substance.	1	2	3	4
	Acid Value.	Saponification Value.	Difference 2-1.	Ratio of 1 : 3. "Ratio number."
Carnaüba wax . .	2	80	78	39
Japan wax . . .	20	227	207	10·8
Chinese wax . . .	Traces	80·4	80·4	...
Spermaceti . . .	,,	130	130	...
Myrtle wax . . .	3	208	205	68·3
Tallow	4	195	191	48
Stearic acid, pure . .	195	195	0	...
,, ,, commercial	200	200	0	...
Rosin, Austrian . .	130-146	146·8-167·1	16·4-21·1	0·126-0·144
,, American . .	154·1-164·6	183·6-194	29·5-30·0	0·191-0·182
Galipot	138	174·6	36·1	0·261
Paraffin wax, ceresin[1] .	0	0	0	...

The acid and saponification values, the means of which have been given already, as also the "ratio numbers," are fairly constant for genuine beeswax collected from all parts of the world. This will be gathered from the following table, in which I have collated a large number of observations, which may be taken as representative of the beeswaxes obtainable from the localities named:—

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[1] Commercial paraffins or ceresin, however, may have a definite acid value.

[Table

Origin.		Number of Samples.	1 Specific Gravity at 15° C.	2 Melting Point. °C.	3 Butyro-refractometer determined at 84° C. calculated to 40° C.	4 Acid Value.	5 Saponification Value.	6 Difference 5-4	7 "Ratio number"	8 Iodine Value.	9 c.c. $\frac{1}{10}$ nor. KOH. required for acids soluble in 80 per cent alcohol.[1]	10 Hydrocarbons. Per cent.	Observer.
Abyssinia, crude		...	0·958	65	...	20·8	93·5	72·7	3·5	...	...	...	Dietze
,, remelted		...	0·958	64·2	...	18·9	94·6	75·7	4·0	...	...	...	,,
,,	Max.	5	...	64·5	44·7	21·00	101·50	80·78	4·03	12·66	5·04	...	Berg
	Min.			63·5	44·5	19·94	96·39	76·40	3·83	10·41	4·14	...	
Algier		28	...	63·5	44·6-44·8	20-20·5	98·5-99·5	78·5-79	3·8-3·9	9-10·5	4·5-4·6	...	,,
Angola		...	0·960	63·5	...	19·6	92·9	73·3	3·7	...	...	...	Dietze
Argentina	Max.	4	...	64·0	44·1	19·89	97·62	78·02	3·96	9·60	3·28	...	Berg
	Min.				43·9	19·39	96·40	76·86	3·85	9·42	3·14	...	
Australia	Max.	4	...	64·5	44·3	19·25	96·95	77·70	4·04	9·71	2·24	...	,,
	Min.			64·0	43·9	18·76	94·64	75·08	4·00	9·23	2·02	...	
Belladi		24	...	64·5	44·2	20·50	95·5-98·5	76·0-78·0	3·6-3·7	8·7-9·5	3·2-3·3	...	,,
Benguela		...	0·961	63	...	19·3	93·1	73·8	3·8	...	...	...	Dietze
,,	Max.	4	...	64·0	45·9	20·58	97·51	77·07	3·80	11·31	4·82	...	Berg
	Min.			63·5	45·2	20·31	97·02	76·93	3·74	10·76	4·79	...	
Bissao		...	0·959	63·5	...	20·9	95·4	74·5	3·6	...	...	...	Dietze
Bissao Wadda	Max.	2	...	65·5	44·8	21·14	99·89	78·89	3·77	11·32	4·48	...	Berg
	Min.			65·0	44·6	20·93	99·82	78·75	3·72	10·68	4·26	...	
Brazil, I.		...	0·962	63·5	...	19·6	89·5	69·9	3·6	...	...	...	Dietze
,, II.		...	0·963	63·5	...	18·3	90·5	72·2	3·9	...	...	...	,,
,,		47	...	65·5	43·5	18·9-19·2	96·0-96·5	76·5-77·5	4·0-4·1	9·0-9·5	2·5-2·6	...	Berg
Caiffa	Max.	2	...	65·5	44·6	20·28	99·26	79·10	3·92	7·98	3·36	...	,,
	Min.			65·0	44·4	20·16	99·10	78·82	3·89	7·39	3·14	...	
California	Max.	5	...	65·5	44·1	19·11	95·31	76·72	3·99	10·76	3·58	...	,,
	Min.			65·0	44·0	18·90	94·15	75·25	3·98	9·60	3·42	...	
Casablanca		...	0·959	63·5	...	18·6	94·8	76·2	4·1	...	...	...	Dietze
,,	Max.	5	...	63·5	44·6	21·14	100·94	81·06	4·08	13·01	5·15	...	Berg
	Min.			63·0	44·4	19·88	99·17	79·17	3·75	9·56	4·93	...	
Chili		...	0·960	65	...	19·7	91·4	71·7	3·6	...	...	...	Dietze
,,		21	...	64·5	43·6	19·5-20·0	94·5-96·0	73·5-76·0	3·7-3·8	7·0	2·9-3·0	...	Berg

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[1] 50 c.c. of filtrate from 5 grms. of beeswax.

Origin.	Number of Samples.	1	2	3	4	5	6	7	8	9	10	Observer.
		Specific Gravity at 15° C.	Melting Point. °C.	Butyro-refractometer determined at 84° C. calculated to 40° C.	Acid Value.	Saponification Value.	Difference 5-4	"Ratio number."	Iodine Value.	c.c. $\frac{1}{10}$ nor. KOH. required for acids soluble in 80 per cent alcohol.[1]	Hydrocarbons. Per cent.	
Chili	...	0·965	...	...	18·81	90·10	71·29	3·79	...	2·00	15·1	Ahrens and Hett
Corsica	1	...	66·5	44·1	19·74	97·79	78·05	3·95	10·82	5·16	...	Berg
Cuba	...	0·961	64	...	20·2	95·2	75·0	3·7	...	...	...	Dietze
,, Max.	3	...	65·0	44·6	19·04	99·89	80·85	4·24	10·98	3·14	...	Berg
Min.			64·0	44·0	18·20	93·24	75·04	4·12	9·46	2·12	...	
Domingo, pale	...	0·962	63·5	...	19·8	93·5	73·7	3·7	...	...	...	Dietze
,, dark	...	0·960	63·5	...	20·3	94·4	74·1	3·65	...	...	...	,,
,, commercial	...	0·960	63·5	...	20·0	93·8	73·8	3·7	...	...	...	,,
,, Max.	5	...	65·0	45·1	21·63	97·79	77·42	3·91	10·82	4·59	...	Berg
Min.			65·0	44·6	19·81	94·64	74·69	3·52	9·84	2·68	...	
,,	...	0·967	...	...	20·11	93·45	73·34	3·65	...	2·69	14·25	Ahr. a. Hett
East Africa, German	...	0·965	64	...	20·0	93·3	73·3	3·9	...	...	...	Dietze
,, ,, Max.	4	...	64·5	44·9	21·56	102·41	80·85	4·16	9·99	5·82	...	Berg
Min.			63·0	44·3	19·39	100·10	76·48	3·75	8·38	4·03	...	
,, ,,	2	0·9489-0·9645	62·2-62·5	...	17·48-18·20	84·34-89·80	66·16-72·32	3·6-4·1	6·1-7·5	...	...	Fendler
Egypt	1	...	63·4	44·0	19·49	97·11	77·62	3·98	7·98	2·80	...	Berg
Germany	...	0·960-0·961	63·5	...	19-22	93-97	72-77	3·7-3·8	...	...	...	Dietze
,,	1427	...	63·5-64·5	44·3-44·7	19·2-20·4	92·0-97·0	72·0-77·0	3·6-3·8	7·5-8·0	2·6-3·3	...	Berg
,, Bayern	...	0·964	...	...	18·67	90·30	71·53	3·84	...	...	15·2	Ahr. a. Hett
,, Hanover	...	0·966	...	...	19·08	91·20	72·12	3·78	...	...	15·2	,,
,, Hessen	...	0·964	...	...	19·15	91·89	72·74	3·80	...	4·70	17·3	,,
,, Holstein	...	0·965	...	...	20·40	93·85	73·45	3·65	...	4·34	15·3	,,
,, Max.	14	...	...	...	20·44	92·35	71·91	3·50	...	...	...	Buchner
Min.					18·29	91·29	73·00	3·99	...	...	..	
Haïti Max.	4	...	65·5	43·9	20·16	97·51	77·42	3·85	9·19	3·02	...	Berg
Min.			64·5	43·9	20·09	93·45	73·29	3·02	8·46	2·13	...	

Italy	77	...	64·5	44·5-44·9	21-21·5	98·0-99·0	75-77·5	3·5-3·8	10·75-12·75	5·0-6·0	...	Berg
Madagascar	...	0·960	64	...	21·1	98·0	76·9	3·65	...	...	...	Dietze
,,	18	...	64·5-65	44·7-45	18·5-19·5	97·0-101·0	78·0-81·0	4·0-4·3	9·0-10·0	4·0-4·5	...	Berg
,,	...	0·970	...	...	20·30	96·80	76·50	3·77	...	5·91	12·8	Ahr. a. Hett
Mazagan, I.	...	0·962	64	...	21·7	102·8	81·0	3·8	...	...	...	Dietze
,, II.	...	0·962	64	...	22·0	102·5	80·5	3·7	...	...	...	,,
Mogador	184	...	63·5	44·4-45·0	19·6-21·5	96·5-98	76·5-78·5	3·8-4·0	10·5-12·0	5·25-4·5	...	Berg
Montenegro	...	0·960	64	...	20·2	92·7	72·5	3·6	...	...	...	Dietze
Morocco	212	...	63·5	44·7-45·2	19·8-21·3	95·5-98·0	75·5-78·5	3·75-3·95	10·5-12·7	5·3-6·1	...	Berg
,,	...	0·968	...	...	20·94	98·89	77·95	3·72	...	3·80	13·2	Ahr. a. Hett
Mozambique	...	0·958	63	...	20·0	94·0	74·0	3·7	...	...	...	Dietze
,,	1	...	64·5	44·7	20·23	101·99	81·76	4·04	11·32	3·58	...	Berg
,,	...	0·967	...	...	18·80	94·90	76·10	4·05	...	3·80	14·1	Ahr. a. Hett
Palenzia	...	...	64·0	44·2	19·40	95·00	75·60	3·80	12·05	4·26	...	Berg
Palestine Max.	3	...	65·5	44·3	21·70	103·69	81·99	3·77	9·65	3·81	...	,,
Min.			65·0	43·9	21·56	102·69	81·13	3·74	9·27	3·36	...	
Poland and Galicia	19	...	63·5	43·2-43·7	19·2-19·5	96·0-97·5	76·5-78·0	3·9-4·0	6·5-6·9	5·2-5·6	...	,,
Portugal	...	0·966	...	...	18·37	91·84	73·47	4·00	...	4·48	15·0	Ahr. a. Hett
,, Max.	17	...	65·5	...	20·53	95·91	77·78	4·30	14·0	3·7	...	Mastbaum
Min.			64·0	...	16·71	88·54	70·49	3·61	6·7	1·1	...	
Sierra Leone	1	...	64·0	44·5	21·28	101·36	80·08	3·76	8·50	3·02	...	Berg
Smyrna	1	...	64·5	44·3	21·28	97·58	76·30	3·58	10·84	3·58	...	,,
Spain Max.	5	...	66·5	44·6	19·67	98·70	79·38	4·11	10·98	3·70	...	,,
Min.			65·5	44·3	19·32	96·04	76·65	3·94	10·76	3·25	...	
Sweden	1	...	63·5	43·9	20·09	96·81	76·72	3·82	9·35	3·02	...	,,
Tangier, I.	...	0·959	63	...	20·6	99·4	78·8	3·8	...	...	...	Dietze
,, II.	...	0·959	63	...	20·6	100·3	79·7	3·9	...	...	...	,,
Tunis	...	0·961	64	...	20·2	95·3	74·9	3·7	...	...	...	,,
,,	1	...	65·0	44·5	18·90	91·28	72·38	3·83	9·72	3·59	...	Berg
Turkey	...	0·965	...	...	19·60	92·18	72·58	3·70	...	3·36	15·0	Ahr. a. Hett
Valdivia Max.	5	...	65·0	43·4	20·30	96·67	77·28	3·98	9·11	2·34	...	Berg
Min.			64·5	42·9	19·59	95·11	75·81	3·87	8·37	2·12	...	
West Africa, German	1	...	65·0	44·4	20·09	96·32	76·23	3·79	10·25	4·36	...	,,
,, ,, ,,	...	0·967	...	...	19·71	92·40	72·69	3·69	...	4·90	13·6	Ahr. a. Hett
Zanzibar	...	0·959	63	...	19·9	94·9	75·0	3·8	...	...	...	Dietze

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[1] 50 c.c. of filtrate from 5 grms. of beeswax.

Most of the "ratio numbers" given in the last table lie in the neighbourhood of 3·8. From these "ratio numbers" the following conclusions may be drawn (*Hübl*): (1) If the saponification value of a sample of beeswax be below 92, whilst the "ratio number" is that of a pure beeswax, then *paraffin wax* or *ceresin* must be present. (2) If the ratio number exceeds 3·8, then an admixture with Japan wax, carnaüba wax, or tallow may be suspected. If the acid value be much below 20, then Japan wax is absent. If, however, the "ratio number" is less than 3·8, then stearic acid or rosin are present. From the foregoing table it will, however, be gathered that the "ratio number" is not so constant as has been assumed by *Hübl*. This is especially shown by the analyses of some genuine waxes which I collate in the following table:—

Origin of Beeswax.	1	2	3	4	Observer.
	Acid Value.	Saponification Value.	Difference 2-1.	"Ratio Number."	
Hungary . .	23	90·6	67·6	2·89	Mangold
Silesia . .	17·8	92·3	74·5	4·2	Weinwurm

It must further be borne in mind that at present artificial combs containing stearic acid are being employed in bee-hives. Hence the acid value of beeswax may be found higher. Beeswaxes obtained from such artificial honeycombs have given acid values from 25 to 26 (*Weinwurm*).

All the foregoing numbers refer to yellow wax. Through bleaching, the yellow wax undergoes some changes which cause great deviations from the normal acid and saponification values. This is illustrated by the numbers I have collated in the following table. They show the changes in the physical and chemical constants which yellow wax suffers on being bleached by various methods:—

	1	2	3	4	5	6	7	8	
	Melting Point.	Acid Value.	Saponification Value.	Difference 3-2	"Ratio number."	Iodine Value.	1 grm. yields Hydrogen.	Hydro-carbons.	Observer.
	°C.						c.c.	Per cent.	
Pure yellow waxes	63-64	19-21	91-95	72-74	3·78-3·52	10-11	52·5-55	13-14	Buisine
Air-bleached waxes, with addition of 3-5 per cent of tallow	63·5-64	21-23	105-115	84-92	4·00-4·00	6-7	53·5-57	11-12	,,
Pure yellow wax	63·5	20·17	93·5	73·33	3·63	10·9	53	13·5	Buisine
Same wax air-bleached, with addition of 5 per cent of oil of turpentine . .	63·5	20·2	100·4	80·2	3·97	6·8	54·9	12·4	,,
Same wax, bleached by hydrogen peroxide	63·5	19·87	98·4	78·53	3·90	6·3	56·1	12·5	,,
Pure yellow wax	63	20·40	95·1	74·70	3·66	11·2	54·5	14·3	Buisine
Same wax, decolourised by animal char. .	63	19·71	93·2	73·49	3·72	11·4	53·6	13·3	,,
,, bleached with permanganate .	63·7	22·63	103·3	80·67	3·56	2·6	...	...	,,
,, ,, ,, .	63·5	21·96	99·2	77·24	3·51	5·8	55·5	13·3	,,
,, ,, bichromate .	63·2	21·86	98·9	77·04	3·52	7·9	51	13·2	,,
,, ,, ,, .	64	23·43	107·7	84·27	3·59	1·1	53·6	11·8	,,
Beeswax, white	...	22·4	98·5	76·1	3·41	...	...	...	Henriques
,, chemically bleached . .	...	24	95	71	2·96	...	...	...	Allen
,, air-bleached	...	19·87	94·82	74·95	3·77	...	...	...	Buchner
,, chemically bleached, I. . .	...	22·02	98·17	76·15	3·45	...	...	...	,,
,, ,, ,, II. . .	...	24·0	98·56	74·56	3·10	...	...	...	,,

A number of analyses of Indian and Chinese beeswaxes are collated in the following table :—

		1	2	3	4	5	6	7	8	9	
Origin.	Number of Samples.	Specific Gravity at 15° C.	Melting Point. °C.	Butyro-refractometer, determined at 84° C. calculated to 40° C.	Acid Value.	Saponification Value.	Difference 5-4	"Ratio number."	Iodine Value.	c.c. $\frac{1}{10}$ norm. KOH. required for acids soluble in 80 per cent alcohol, by Buchner's process.	Observer.
East India[1] . . .	...	...	65	...	6·10	83·30	77·20	12·1	10	...	Buchner
		...	66	...	6·01	82·12	76·11	12·6	10	...	,,
,, ,, . Max.	418	...	63·5	44·8	8·96	106·10	99·45	14·95	9·29	3·00	Berg
Min.		...	63·5	44·1	6·30	93·59	86·24	10·00	7·16	2·25-2·75	
Mean		...	63·0	44·3-44·7	7·0-7·5	96·0-101·5	89·0-94·0	12·5-13·5	8·5-8·7	2·02	
Tonkin and Cochin-china Max.	281	...	63·5	45·1	8·41	97·02	89·88	12·33	9·07	3·58	,,
Min.		...	63·0	44·7	7·21	93·27	85·73	11·40	6·96	2·67	
China . . Max.	4	...	66·5	45·5	9·52	105·07	96·88	10·02	12·17	6·16	,,
Min.		...	66·0	45·4	9·03	104·37	94·85	9·96	11·98	6·08	
,, ...	...	...	66	...	7·55	93·70	86·15	11·4	...	...	Buchner
,, ...	...	...	62-63	...	5·33	95·61	90·28	17·9	...	...	,,
Max.	...	...	...	...	8·72	120·17	111·45	12·78	...	...	,,
Min.		...	...	...	6·28	90·20	83·82	13·9	...	...	,,

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[1] To this class of waxes belongs the wax known in commerce as "Ghedda wax."

These beeswaxes were considered as "abnormal" since no adulterants could be detected by the usual tests. In my opinion, however, some of these waxes seem to be mixtures of genuine beeswax with (Chinese) insect wax.[1] At least, in the case of a sample of Chinese beeswax submitted to me for examination I was able to prove that adulteration with (Chinese) insect wax had taken place. The results of this examination are given in the following table:—

Specific Gravity at 15°.	Acid Value.	Saponification Value.	"Ratio Number."	Iodine Value.
0·9392	9·01	87·62	8·73	11·53
At 90°.				
0·8555				

The determination of the acid and saponification values alone is not sufficient proof of the purity of a beeswax, as it is easy to prepare mixtures having a normal "ratio number" and yet containing no beeswax whatever. This will be gathered from the following table, which gives the acid and saponification values for a mixture consisting of 37·5 parts of Japan wax, 6·5 parts of stearic acid, and 56 parts of ceresin or paraffin wax.

.	1	2	3	4	5	6	7	8	9
						Conditioning.			
	Acid Value.	Saponification Value.	Difference. 2-1	"Ratio Number."	Parts in 100.	Acid Value.	Saponification Value.	Difference. 7-6	"Ratio Number."
Japan wax . .	20	220	200	10	37·5	7·5	84·5	75	10
Stearic acid . .	195	195	0	...	6·5	12·7	12·7	0	...
Ceresin, paraffin wax	0	0	0	...	56·0	0	0	0	...
Mixture . .						20·2	95·2	75	3·71

The ratio number of this mixture would be 3·71. It is evident that indefinite quantities of the above mixture, or of a similarly prepared one, might be admixed with wax without being detected by the determination of the acid and saponification values.

The determination of the iodine value is of somewhat secondary

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[1] It should be pointed out that the iodine values of the samples in the table are remarkably high, in the view of the fact that the iodine value of (Chinese) insect wax is very low.

importance in the examination of beeswax; still, it will assist in the interpretation of the results obtained by other methods, and in the detection of certain impurities.

In doubtful cases further examination is required, and the following tests are recommended:—

Detection and Determination of Glycerides.—Although in most cases the presence of glycerides will be detected by a higher saponification value than the normal one, still small quantities may be introduced by means of a judiciously-prepared mixture of glycerides, stearic acid, and paraffin wax or ceresin. The absence of glycerides can only then be pronounced with certainty if no glycerol is found. The safest plan is to determine the amount of glycerol quantitatively by working with at least 20 grms. of the suspected wax. The qualitative test for glycerol is too delicate, since small quantities, say 2 to 3 per cent of a glyceride, which may have been admixed with a yellow wax before bleaching (as is usually done on a manufacturing scale), may give a positive reaction in the acroleïn test, and thus lead to erroneous conclusions unless they be confirmed by the quantitative tests. The amount of glycerol multiplied by 10 gives approximately the percentage of added glyceride.

Detection of Stearic Acid.—Considerable quantities of stearic acid are readily detected by a high acid value of the sample, provided no compensating substances like ceresin and paraffin wax have been added. It should be borne in mind that colophony also raises the acid value (for the detection of rosin, see below). If in consequence of added paraffin wax or ceresin a normal acid value has been found, and yet stearic acid be suspected, then one of the following methods must be resorted to. They are based on the principle that on treating a sample with boiling alcohol any stearic acid present will be dissolved together with cerotic acid, but will not separate out so completely as the latter does on cooling. The following process has been suggested by *Fehling*,[1] and recommended by *Röttger*:[2] 1 grm. of the sample is boiled for a few minutes with 10 c.c. of 80 per cent alcohol; after cooling, the alcoholic solution is filtered and the filtrate mixed with water. In the case of a pure wax the liquid is perfectly clear, or is only slightly opalescent, but in case it be adulterated with stearic acid, it loses its transparency, and flocks of separated stearic acid rise to the top. This reaction is plainly perceptible even if the adulteration amount to as little as 1 per cent of stearic acid. It should be borne in mind that also rosin, if present, will be dissolved and give an emulsion with water.

Jean[3] endeavours to determine the stearic acid quantitatively by heating 3 to 4 grms. of the sample with 60 c.c. of 96 per cent alcohol to boiling, allowing the solution to cool, and titrating with half-normal alkali, using phenolphthalein as an indicator. The alkali used is calculated to stearic acid.

In the presence of rosin the determination would include the

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[1] *Dingl. Polyt. Journ.* 147, 227.

[2] *Journ. Soc. Chem. Ind.* 1890, 771.

[3] *Ibid.* 1891, 728.

amount of alkali required to neutralise the rosin acids. A combination of these two tests has been more fully worked out by *Buchner.*[1] He proceeds in the following manner: 5 grms. of the sample are placed in a round-bottomed flask and 100 c.c. of 80 per cent alcohol (prepared from 850 c.c. 96 per cent alcohol and 190 c.c. of water) are added. The total weight of the flask and contents is then ascertained. Next the contents of the flask are heated until the mass boils gently and are kept at this temperature for 5 minutes, with frequent shaking. The flask is then immersed in cold water whilst being constantly shaken and allowed to cool down to the ordinary temperature. The flask is weighed again and brought up to the original weight by the addition of 80 per cent alcohol. The liquid is then filtered through a plaited filter, and 50 c.c. of the filtrate are titrated with $\frac{1}{10}$ normal alcoholic potash, phenolphthalein being used as an indicator. By proceeding in this manner *Buchner* ascertained the following acid values :—

	c.c. $\frac{1}{10}$ nor. KOH. required for acids soluble in 80 per cent alcohol. 50 c.c. of alcohol from 5 grms. of beeswax.
Pure beeswax, yellow	3·6-3·9
,, ,, white	3·7-4·1
Palm wax	1·7-1·8
Carnaüba wax	0·76-0·87
Japan tallow (Japan wax)	14·93-15·3
Rosin	150·3
Stearic acid	65·8
Tallow "stearine"	1·1
"Artificial waxes," having the "ratio numbers" of normal beeswax—	
I. Consisting of stearic acid, tallow stearine, and ceresin	21·40
II. Consisting of stearic acid, Japan tallow, and ceresin	17·80
III. Consisting of rosin, tallow stearine, and ceresine	22·0
Pure beeswax, containing 25 per cent "Artificial wax" I.	8·4
,, ,, containing 50 per cent ,, ,, II.	11·3

Berg,[2] who has examined a very large number of waxes by *Buchner's* method (see table, p. 891), points out that the alcoholic solution made up as described above must be allowed to stand 12 hours, as otherwise the results are discordant, and generally too high. Unless a sample be allowed to stand 12 hours, the acids dissolved by the 80 per cent alcohol are found too high by 20 to 30 per cent. It should be further pointed out that the detection of stearic acid in bleached waxes, if present only to the extent of 1 to 3 per cent, is very difficult, as chemically bleached waxes may retain small amounts of acid substances.[3]

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[1] *Chem. Zeit.* 1895, 1422.

[2] *Ibid.* 1903, 754.

[3] Thus Medicus and Wallenstein (*Zeit. Unters. Nahrgs. u. Genussm.* 1902, 1092) showed that the acid value of a beeswax bleached with bichromate and sulphuric acid was as high as 24·7.

In doubtful cases it would perhaps be advisable to use larger quantities and separate the stearic acid as such. It should, however, be remembered that commercial stearic acid, such as would be used for adulteration, is not pure stearic acid (cp. chap. xv.).

Detection of Ceresin and Paraffin Wax.—The examination of beeswax by the saponification process can only reveal the presence of ceresin and paraffin wax down to 10 or 8 per cent, if no other adulterant be present. If the admixture falls below 5 or even below 8 per cent, the deviations from the normal acid and saponification values become so small that by these two tests alone adulteration cannot be detected. An excellent preliminary test for the detection of added ceresin and paraffin wax down to 3 per cent has been proposed as a qualitative test by *Weinwurm.*[1] This qualitative test is based on the fact that a hot aqueous glycerin solution dissolves the unsaponifiable matter of beeswax, whereas ceresin and paraffin wax are insoluble in it. The process is carried out as follows:—Saponify 5 grms. of the sample with 25 c.c. half-normal alcoholic potash, evaporate off the alcohol, add 20 c.c. of conc. glycerin, heat on the water-bath until solution is effected, and then run in 100 c.c. of boiling water. Pure beeswax gives a more or less clear, transparent, or translucent mass, through which ordinary print can be read easily. If 5 per cent of hydrocarbons are admixed, the solution is cloudy, and the print is no longer legible; in the case of 8 per cent a precipitate is obtained.

I have examined this process in my laboratory, and can recommend it as a reliable preliminary test for *pure beeswax.* Turbidity of the solution does not, however, solely indicate the presence of added ceresin or paraffin wax, since also carnaüba wax and insect wax give a turbid solution. Mixtures prepared from pure beeswax and carnaüba wax, as also mixtures from pure beeswax and (Chinese) insect wax, give as strong a turbidity as does pure beeswax containing 5 per cent of paraffin wax (*Lewkowitsch*).

The specific gravity test will only reveal considerable quantities of added ceresin and paraffin wax, and cannot therefore be assigned discriminative importance. In special cases, however, the following tables may prove of some little value:—

Specific Gravity of Mixtures of Beeswax and Paraffin Wax (Wagner)[2]

Beeswax.	Paraffin Wax.	Specific Gravity.
Per cent.	Per cent.	
0	100	0·871
25	75	0·893
50	50	0·920
75	25	0·942
80	20	0·948
100	0	0·969

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[1] *Chem. Zeit.* 1897, 519.

[2] *Zeitsch. f. analyt. Chem.* 5, 280.

Specific Gravity of Mixtures of Beeswax and Ceresin (*Dieterich*)[1]

Yellow Wax.	Yellow Ceresin.	Spec. Grav. of Mixture.	White Wax.	White Ceresin.	Spec. Grav. of Mixture.
Per cent.	Per cent.		Per cent.	Per cent.	
100	0	0·963	100	0	0·973
90	10	0·961	90	10	0·968
80	20	0·9575	80	20	0·962
70	30	0·953	70	30	0·956
60	40	0·950	60	40	0·954
50	50	0·944	50	50	0·946
40	60	0·937	40	60	0·938
30	70	0·933	30	70	0·934
20	80	0·931	20	80	0·932
10	90	0·929	10	90	0·930
0	100	0·922	0	100	0·918

Considerable quantities of added ceresin and paraffin wax may be detected by the determination of the unsaponifiable matter, *i.e.* alcohols + hydrocarbons. It has been pointed out already that the unsaponifiable portion must be determined with certain precautions which are detailed on page 297. Strictly quantitative results cannot be expected, since the amount of "unsaponifiable" in different beeswaxes varies within too wide limits. The numbers given in the table of constants fluctuate between 52·38 and 55·58. *Werder*[2] arrived, in the examination of 21 samples of beeswax, at numbers lying between 48·55 and 53·08 per cent. In view of the tediousness of this process, and the uncertainty of the conclusions to be derived therefrom, it cannot be recommended for the quantitative estimation of added ceresin and paraffin wax.

The proportion of total hydrocarbons in beeswax is accurately determined by *A. & P. Buisine's* process (p. 381). 2 to 10 grms. of the sample are heated with potash-lime to 250° C., the residue is powdered, and extracted in a Soxhlet extractor with dry ether or dry petroleum ether. The extract is filtered, if necessary, the solvent evaporated off, and the residue dried and weighed. The proportion of hydrocarbons in genuine yellow beeswax varies, according to *Buisine*, from 12·7 to 13 per cent, and according to *Kebler*, from 12·5 to 14·5 per cent.

Adulteration with 3 per cent of foreign hydrocarbons can be detected, as an easy calculation will show. The liberated hydrogen may also be measured and calculated to myricyl alcohol. 1 grm. of pure beeswax should yield from 53·5-57·5 c.c. of hydrogen, corresponding to 52·5-56·5 per cent of myricyl alcohol. In case the latter be not required, the apparatus for collecting and measuring the gas need not be employed.

More recent determinations by *Ahrens* and *Hett* have, however, shown that the amount of hydrocarbons may rise up to 17·3 per

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[1] Wagner's *Jahresbericht*, 1882, 1028.

[2] *Chem. Zeit.* 1900, 967.

cent (cp. table, p. 892), so that the certainty afforded hitherto by *Buisine's* test for the detection of 3 per cent of hydrocarbons becomes somewhat illusory. For some alterations in *Buisine's* arrangement of apparatus, proposed by *Ahrens* and *Hett*, the reader may be referred to the original paper, and it need only be pointed out that for the successful carrying out of *Buisine's* test the potassium hydrate should not be finely powdered, since a fine powder is apt to form lumps when the wax is poured over it. Thus unattacked wax may rise in the tube and escape decomposition.

The melting points and iodine values of the hydrocarbons contained in pure beeswax are collated in the following table :—

Melting Point.	Iodine Value.	Observer.
° C.		
49·5	22·05	A. & P. Buisine
51·0	22·5	Mangold
55·2	20·1	Ahrens and Hett

Detection of Wool Fat and Wool Wax.—The presence of wool fat or wool wax is best recognised by testing the alcohols for cholesterol or isocholesterol. Since I have shown (p. 379) that cholesterol can be recovered practically completely from the potash-lime used in *Buisine's* process, the safest plan is to convert the alcohols into acids, and examine the extracted hydrocarbons for cholesterol.

Detection of Rosin.—The presence of rosin is detected with certainty by the *Liebermann-Storch* colour test. In the case of a dark coloured wax it is advisable to extract the wax with alcohol, and test the residue obtained after evaporating the alcohol. If a 50 per cent alcohol be used and the alcoholic solution be filtered in the cold, stearic acid, if present, is not extracted. Approximately quantitative results are therefore obtainable if the residue obtained after evaporating off the 50 per cent alcohol be weighed. More accurate results are obtained by determining the rosin in the alcoholic extract by *Twitchell's* method.

Detection of Carnaüba Wax.—Considerable quantities of carnaüba wax may be detected qualitatively by the refractometric test and the chloroform test (see p. 886). The best preliminary test, however, is, in the absence of mineral waxes and insect wax, *Weinwurm's* test, as I have ascertained by experiments in my laboratory. According to *Berg*, mixtures of beeswax and carnaüba wax commence to melt at 68°-70° C., and are not completely melted at 79°-80° C. From the "ratio number" of the wax conclusions can be drawn as to the presence of carnaüba wax, provided other adulterants, influencing the ratio number in the same manner, be absent. If they be present, a thorough examination of the neutral esters is required. The quantitative determination of carnaüba wax in beeswax is a very difficult problem, and can only be solved with sufficient accuracy by an exhaustive examination of both the free and combined fatty acids.

Detection of Insect Wax.—As a preliminary test for the detection of insect wax, in the absence of mineral waxes and carnaüba wax, the *Weinwurm* test can be recommended. If insect wax be the only adulterant then its presence will be detected by an abnormally high "ratio number." It has been pointed out above (p. 897) that in a sample so adulterated the iodine value 11·5 was found. As insect wax ought to have lowered the iodine value of the adulterated sample considerably, some other foreign substance must have been added (perilla oil?) It is evident that the detection of insect wax offers similar difficulties as the detection of carnaüba wax. In doubtful cases the problem can only be solved by a thorough examination of the neutral esters.

SPERMACETI (CETIN)

French—*Blanc de Baleine*. German—*Walrat*.
Italian—*Spermaceto*.

For table of constants see p. 904.

Spermaceti (cetin) occurs chiefly in the head cavities and in the blubber of the sperm whale, *Physeter macrocephalus* (cp. p. 865), and the bottlenose whale, *Hyperoödon rostratus;* it has been also found in somewhat smaller quantities in other *cetacea;* it constitutes the solid portion of dolphin oil (p. 679) and of shark oil. The mode of preparing spermaceti has been described above, p. 866. Crude sperm oil yields about 11 per cent of spermaceti.

Refined spermaceti forms lustrous, white, translucent masses with a broad leafy crystalline structure; it is so brittle that it can be rubbed to powder; it is almost without taste and odour. In the melted state it leaves a grease-spot on paper. It is insoluble in cold 90 per cent alcohol, and sparingly soluble in 96 per cent alcohol. It dissolves, however, easily in boiling alcohol (1 part in 40 parts); on cooling, the bulk separates in a crystalline condition.

Chemically, spermaceti consists chiefly of cetin,[1] *i.e.* cetyl palmitate. Since the saponification value of pure cetin is 116·9, it is evident that other esters must occur in spermaceti. The statement[2] that spermaceti contains also glycerides of lauric, myristic, and stearic acids as normal constituents requires confirmation. *Lewkowitsch*[3] found in a commercial sample, of the saponification value 122·3, the acetyl value 23·3; this would point to the presence of a small amount of free alcohols. By crystallisation from alcohol pure cetin is obtained.

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[1] The requirements of the U.S.Ph. appear to correspond rather with the numbers required for cetin than those for spermaceti; cp. L. Kebler, *Journ. Soc. Chem. Ind.* 1896, 206.

[2] Heintz, *Liebig's Annalen*, 92. 291.

[3] *Analyst*, 1899, 321.

Physical and Chemical Constants of Spermaceti

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.	
At C.		Observer.	C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.
15	0·960	Dieterich	43·4-44·2	Rüdorff	43·5-44·1	Rüdorff	128	Allen
,,	0·905-0·945	Kebler	48	Allen	49	Allen	125·8-134·6	Kebler
60	0·8358	Allen	42-47	Kebler	45	Barfoed	130·6-131·4	Henriques
(water at 15·1 = 1)					42-44·5	Kebler	122·7-130·1	Lewkowitsch
98-99	0·8086-0·812	Allen						
(water at 15·1 = 1)	0·8082-0·816	Kebler						

Physical and Chemical Constants of Spermaceti—continued

Alcohols.		Fatty Acids.		Iodine Value.	
Per cent.	Observer.	Per cent.	Observer.	Per cent.	Observer.
51·48	Allen	53·45	Lewkowitsch	3·8	Lewkowitsch
51·41	Lewkowitsch				

On examining *commercial* samples, the writer found iodine absorptions of 3·52 to 4·09, no doubt due to small quantities of sperm oil adhering to the spermaceti. If other iodine-absorbing impurities (tallow) are absent, the proportion of sperm oil may be calculated, adopting 82·5 as the iodine value of the latter.

The esters in spermaceti are readily saponified by boiling with alcoholic potash; on diluting the alcoholic solution with water, cetyl alcohol is precipitated.

Spermaceti cannot be easily adulterated, as any foreign substance causes it to lose its physical characters, such as transparency and crystalline structure. Genuine samples of commercial spermaceti contain small quantities of free fatty acids only. Thus *Lewkowitsch* found in a commercial sample the acid value 1·35, and *Kebler* in the examination of twelve samples of spermaceti acid values ranging from 0·09 to 0·47.

A higher acid value of a sample would indicate the presence of *stearic acid* or *beeswax;* a high iodine value that of *tallow.* These substances would also be pointed out by abnormal saponification values. They may be detected, as also may *paraffin wax,* by the methods described under "Beeswax."

A rapid process for the detection of *stearic acid*[1] is to melt the sample in a porcelain basin, and to stir it well with a few c.c. of ammonia. After cooling, the solidified cake is removed and the aqueous solution acidified, when stearic acid separates. The presence of even 1 per cent of stearic acid may be thus ascertained.

Spermaceti is employed exclusively in the manufacture of sperm candles (see chap. xv.).

INSECT WAX, CHINESE WAX

French—*Cire d'insectes.* German—*Insektenwachs, Chinesisches Wachs.*
Italian—*Cera d'insetti.*

For table of constants see p. 907.

Insect wax is the secretion of an insect, *Coccus ceriferus,* Fabr., or *Coccus pela,* Westwood.

The larvæ of the insect appear early in the spring on the bark, boughs, and twigs of *Ligustrum lucidum* (the "evergreen" tree growing in Western China, in the Chien-Chang valley, near the Thibetan frontier) in the form of numerous brown, pea-shaped scales. These scales are gathered by the natives about the end of April, wrapped carefully in packages, each containing about 1 lb., so as to protect the larvæ from the heat whilst these packages are

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[1] *Les Corps gras industriels,* 13. 207.

being carried to Chia-ting, the centre of the insect wax industry, a distance of about 200 miles from the Chien-Chang valley. Here each package is made up into smaller packages wrapped in leaves, and suspended under the branches of a species of ash, most likely *Fraxinus Chinensis*, after holes have been made in the leaves which cover the larvæ. On emerging from the scales, the insects creep up the branches to the leaves of the tree, among which they remain thirteen days. They then descend to the branches and twigs, where the insect wax is secreted. The first appearance of the wax on the undersides of the boughs and twigs resembles snow; it gradually spreads over the whole branch to the depth of about a quarter of an inch. Three months after the placing of the insects on the tree the branches are cut off, and as much wax as possible is removed by hand. In order to recover a further quantity the branches are boiled with water. In consequence of this the larvæ are destroyed, and hence fresh scales must be brought the following year for another crop of wax. One pound of scales is stated to produce four to five pounds of wax (*Hosie*).

This wax has a yellowish-white colour; it is odourless and tasteless, has a lustrous appearance and a crystalline structure. It resembles spermaceti in appearance; it is, however, more fibrous and considerably harder, so much so that it can almost be powdered.

Insect wax is very slightly soluble in alcohol and ether, but easily soluble in benzene, from which it can be obtained in a crystalline form. It consists chiefly of ceryl cerotate, $C_{26}H_{53}.C_{26}H_{51}O_2$, which can be readily obtained from the wax by repeated crystallisation from petroleum ether (boiling point 115°-135° C.) Since the theoretical saponification value of ceryl cerotate is 73·8, other esters must be admixed with the ceryl cerotate, as the saponification values of commercial samples are considerably higher. Owing to the separation of potassium cerotate during saponification and titration, low saponification values were found by earlier observers; these lower numbers are omitted here. A commercial sample of Chinese wax examined by the writer absorbed 1·4 per cent of iodine. Another sample had the acid value 1·5. In the *Weinwurm* test (see p. 900) Chinese wax behaves like beeswax adulterated with paraffin wax (*Lewkowitsch*).

Insect wax is used in China and Japan for making candles, for polishing furniture and leather, and as a sizing material for paper and cotton goods. On account of its extensive use in its home it is not largely exported to Europe.[1]

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[1] *Journ. Soc. Chem. Ind.* 1897, 685.

[TABLE

Physical and Chemical Constants of Insect Wax

Specific Gravity.			Solidifying Point.		Melting Point.		Saponification Value.		Fatty Acids.		Alcohols.		Iodine Value.	
At °C.		Observer.	°C.	Observer.	°C.	Observer.	Mgrms. KOH.	Observer.	Per cent.	Observer.	Per cent.	Observer.	Per cent.	Observer.
15	0·926	Gehe	80·5-81	Allen	80·5-81	Allen	93	Henriques	51·54	Lewkowitsch	49·51	Lewkowitsch	1·4	Lewkowitsch
15	0·970	Allen			81·5-83	Henriques	80·5	,,						
99 (water 15·5=1)	0·810	,,					91·65	Lewkowitsch						
							80·4	,,						

Psylla Wax [1]

This wax is secreted by *Psylla Alni*, an aphide living on the leaves of *Alnus incana*. It is obtained by extracting the insects first with hot ether in order to remove the glycerides, and finally with hot chloroform.

The wax is insoluble in hot ether, and only sparingly soluble in cold chloroform, but readily soluble in hot chloroform and benzene. It crystallises in needles of silky lustre, melting at 96° C.

Psylla wax is the psyllostearylic ester of psyllostearylic alcohol (see pp. 99 and 130).

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[1] Sundwick, *Zeit. phys. Chem.* 1901 (32), 355.

[Table

LESSER KNOWN ANIMAL WAXES

Wax from		Number of Samples.	Specific Gravity at 15° C.	Melting Point. °C.	Butyro-refractometer determined at 84° C. calculated to 40° C.	Acid Value.	Saponification Value.	Difference, 5-4.	"Ratio Number."	Iodine Value.	c.c. $\frac{1}{10}$ norm. KOH. required for Acids soluble in 80 per cent Alcohol	Hydrocarbons. Per cent.	Observer.
Bumble bee	Max.	19	...	63·0	51·6	19·39	95·90	76·65	4·00	16·10	9·18	...	Berg
	Mean		...	62·0	50·0-51·0	19·0-19·2	95·0-95·5	76·0-76·5	3·95-4·0	15·8-15·9	5·0-7·0	...	
	Min.		...	62·0	49·5	18·41	92·12	73·71	3·93	15·76	4·92	...	
,, ,,		...	0·973	...	...	7·8	48·3	40·5	5·2	...	...	25·1	Ahrens a. Hett
Cicade wax—I.		...	0·965	...	...	7·8	95·9	88·1	11·29	...	...	10·6	,,
,, ,, II.		...	0·965	...	...	7·3	97·95	90·65	12·41	...	...	8·2	,,
Ceroplastes ceriferus—													
Expressed		...	1·04	60									
Extracted		...	...	55									
Ceroplastes rubeus—													
Expressed		...	1·03 at 23° C.	60									
Extracted		...	...	55									

Cochineal wax from *Coccus cacti* consists of coccceryl coccerate.

CHAPTER XV

TECHNOLOGY OF OILS, FATS, AND WAXES

Technical and Commercial Examination of the Products of the Oil and Fat Industries

THE oils, fats, and waxes described in the preceding chapter form the raw materials of the oil and fat industries.

Since the supply of natural oils and fats is well-nigh inexhaustible, their technical preparation by synthetical methods has no practical importance,[1] except in the case of *acetin*, the triglyceride of acetic acid.

ACETINE

ACETINE is used as a solvent (possessing certain advantages over other solvents, such as alcohol, etc.) for indulin and other colouring matters employed by the calico printer as a steam colour.

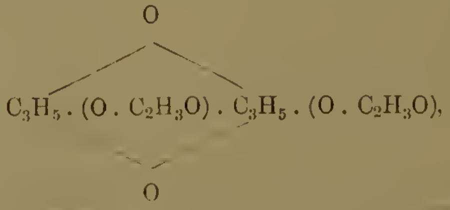
More recently it has been employed as an adulterant of peppermint oil.

Commercial "acetine" is prepared by heating together glycerin and glacial acetic acid (p. 10).

As *Geitel*[2] has shown, there are always formed simultaneously triacetin, diacetin, and monoacetin in variable quantities, depending on the special conditions of each experiment, whilst a certain amount of glycerol remains unattacked. Furthermore, the several acetins react with glycerol to form products of condensation, such as monoacetyldiglycerol

$$C_3H_5 . (OH)_2 - O - C_3H_5 . (O . C_2H_3O) . OH,$$

and diacetyldiglycid



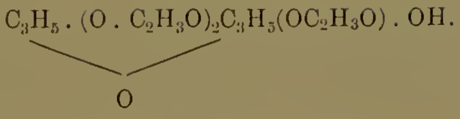
$$\underset{O}{\overset{O}{C_3H_5 . (O . C_2H_3O) . C_3H_5 . (O . C_2H_3O),}}$$

---

[1] Cp. Lewkowitsch, "Problems in the Fat Industry," *Journ. Soc. Chem. Ind.* 1903. 592. The synthesis of the mono-, di-, and triglycerides, carried out hitherto on a laboratory scale, has been described in Chapter I.

[2] *Journ. f. prakt. Chemie*, 1897 (55), 428.

and triacetyldiglycerol



$$C_3H_5 . (O . C_2H_3O)_2C_3H_5(OC_2H_3O) . OH.$$

For purposes of practical analysis, however, it may be assumed that commercial acetine consists of a mixture of diacetin and triacetin. Besides these, the commercial preparations contain free acetic acid and water.

The proportions of diacetin and triacetin are found by estimating on the one hand the combined acetic acid, and on the other hand the glycerol by the acetin process (see p. 286). The analysis is carried out as follows :—

An accurately weighed quantity of the sample is neutralised with half-normal aqueous potash, using phenolphthalein as an indicator. Thus the *free acetic acid* is obtained. Then run into the neutralised solution a measured quantity of caustic soda of 1·1 specific gravity, the strength of which is ascertained by titrating with half-normal hydrochloric acid, and boil for half an hour, whereby the diacetin and triacetin are saponified, the liberated acetic acid combining with caustic soda. After titrating back the excess of caustic soda with half-normal hydrochloric acid, the number of c.c. of half-normal caustic soda used for 1 grm. of substance is found.

A fresh quantity—about 1·5 to 2 grms.—of the sample is then weighed off accurately and the glycerol determined as described p. 286. The proportion of water is found by difference.

Suppose 1 grm. of the sample required 2 c.c. of half-normal caustic soda for neutralisation, then the sample contains $\frac{2 \times 3\text{[1]}}{2} = 3$ per cent of *free acetic acid*. Let the number of c.c. of half-normal caustic soda required to neutralise the acetic acid formed on saponifying (*combined acetic acid*) in *one* gram be 20 c.c., and the percentage of glycerol found be 33·3 per cent. It is convenient to calculate the *combined* acetic acid to C_2H_2O (42), as the sum of the percentages of C_2H_2O and of glycerol equals the sum of the diacetin and triacetin in the sample. The proportion of combined C_2H_2O is $20 \times 2{\cdot}1 = 42$ per cent. Let x and y be the percentages of diacetin and triacetin respectively, then we have

$$x + y = 42 + 33{\cdot}3 = 75{\cdot}3 \quad . \quad . \quad . \quad . \quad . \quad (1).$$

One molecule of diacetin, or 176 parts, yields 92 parts of glycerol; one molecule of triacetin, or 218 parts, also yields 92 parts of glycerol, hence

$$\frac{92x}{176} + \frac{92y}{218} = 33{\cdot}3 \quad . \quad . \quad . \quad . \quad . \quad (2).$$

From equations (1) and (2) we find $x = 60{\cdot}12$ and $y = 15{\cdot}18$. The sample has, therefore, the following composition :—

---

[1] Acetic acid $C_2H_4O_2 = 60$.

Diacetin	60·12 per cent.
Triacetin	15·18 ,, ,,
Acetic acid	3·00 ,, ,,
Water (by difference)	21·70 ,, ,,
	100·00

A convenient classification of the oil and fat industries may be arranged under the following three heads :—

A. INDUSTRIES HAVING FOR THEIR OBJECT THE REFINING OF OILS AND FATS.

B. INDUSTRIES IN WHICH THE GLYCERIDES UNDERGO A CHEMICAL CHANGE, BUT ARE NOT SAPONIFIED.

C. INDUSTRIES BASED ON THE SAPONIFICATION OF OILS AND FATS.

The industries dealing with *waste fats* will be considered in Chapter XVI., although the operations practised in these industries fall under one or more of the three foregoing headings.

A.—INDUSTRIES HAVING FOR THEIR OBJECT THE REFINING OF OILS AND FATS

The general methods of refining and bleaching have been outlined already in Chapter XIII. Those methods which apply to individual oils and fats have been considered in the last chapter under the separate heading of each oil and fat which is refined on a commercial scale. The method of refining and the degree to which it is carried depend, of course, on the purpose which the oils and fats are intended to serve. Therefore, the methods must be adapted to each individual case, as has been pointed out already.

I. EDIBLE OILS AND FATS

Oils and fats which are intended to serve as food are chiefly refined by physical methods. Chemicals involving the use of mineral acids must be altogether excluded from the purview of the refiner, since the mineral acids, however carefully they may be removed by subsequent washing, impart an objectionable flavour to the products treated, thus rendering them useless for edible purposes. Alkalis or alkaline earths are not so objectionable, and are therefore used commercially in the refining of edible oils and fats. A notable example of this kind is the refining of cotton seed oil. The *physical* methods consist in boiling with water or treating with steam, followed by filtration, to remove the last traces of moisture and of suspended matter. If it be required to remove small amounts of colouring matter, the materials are treated with charcoal or fuller's earth, and filtered through a filter-press under pressure.

1. EDIBLE OILS, SALAD OILS, SWEET OILS

French—*Huiles comestibles.* German—*Speiseöle, Tafeloele.*
Italian—*Olii di tavola.*

Most of the vegetable cold drawn oils, if prepared from fresh seeds or fruits, are suitable for edible purposes, as also for the preservation of food stuffs (*e.g.* olive oil in the sardine tinning industry). Hence, practically every vegetable oil, provided it contain no toxic substances (castor oil, croton oil), may be, and indeed is so employed, as has been pointed out already in Chapter XIV. Naturally, much depends on the palatableness of the oil. Hence, whereas rape oil and linseed oil find a ready market for edible purposes in India, these oils are only used in exceptional cases in Western Europe. Their place is taken in richer countries by poppy seed oil, cotton seed oil, sesamé oil, arachis oil, and olive oil.

The chief attention in the manufacture of edible oils must be devoted to the removal of free fatty acids. For this purpose alkalis and alkaline earths are almost exclusively used. Conjointly with the free fatty acids there are also removed natural impurities, such as mucilaginous and albuminoid substances, which are instrumental in bringing about hydrolysis (chap. i. p. 23) and thus give rise to the formation of free fatty acids and rancidity, which follows in the wake of hydrolysis.

It is of great importance that edible oils should not congeal at temperatures near the freezing point. Olive oil practically fulfils this demand, with the exception of some Tunisian olive oils (from Sfax, Sousse, Mahdia, Monastir, see chap. xiv. p. 625), which must be "demargarinated" in the same manner as is cotton seed oil (see below) before it can be placed on the market.

Arachis oil stands in this respect midway between olive oil and cotton seed oil (cp. "Arachis Oil," p. 599). From cotton seed oil, which is at present used in enormous quantities as an edible oil (as also for adulterating high-class edible oils), a considerable portion of "stearine" separates out at a temperature of about 40° F. In order to render cotton seed oil suitable as a table oil, *i.e.* to produce a "winter oil" (chapter xiv.), the "stearine" must be removed, or, as the technical term runs, the oil must be "demargarinated." Originally the process of demargarination consisted in simply storing the oil in large vessels during the winter, when the "stearine" settled out as a solid mass at the bottom of the vessels, so that the supernatant clear oil, freed from most of the stearine, could be drawn off. This process seems to be still in operation in the case of arachis oil (p. 599). Owing to the large amount of capital locked up, this process would be too expensive for cotton seed oil, enormous quantities of which are required by the market. Hence, in modern establishments the oil is refrigerated artificially, and the "stearine" removed by filtering or pressing.

In commerce "edible oil," or "table oil," no longer denotes any one oil, unless it be specifically sold as such. It frequently represents a "blend" of several edible oils, such as cotton seed, sesamé, arachis, and olive oils. Hence, a blend of the kind just mentioned cannot be termed adulterated olive oil unless it has been sold as olive oil. Table oils sold under fancy names are, as a rule, "blends."

The examination of the individual oils and the detection of adulterants has been treated at length in the foregoing chapter.

After the nature of an edible oil has been ascertained (*i.e.* whether free from adulterants,[1] if it be sold as a specific oil), the estimation of the free fatty acids is required to complete the examination.

No rule can be laid down as to what should constitute the permissible maximum of free fatty acids in a salad oil or culinary oil (for frying fish), the limit naturally depending on the demand as to taste and palatableness made in various countries or localities.

It may, however, be stated that a perfectly neutral oil has an insipid taste, and that therefore an oil must not be judged unsuitable for edible purposes for the single reason that it contains about 1 per cent of free fatty acids. Edible cotton seed oil being refined by means of alkalis or alkaline earths will usually be found to contain much less than 1 per cent of free fatty acids.

2. EDIBLE FATS

French—*Graisses comestibles.* German—*Speisefette, Kunstspeisefette.*
Italian—*Grassi di tavola.*

Such edible fats as suet (tallow), butter, cacao butter, goose fat, etc., rarely undergo a process of technical purification before they are placed on the market. Here only those edible fats will be considered which are prepared on a manufacturing scale as substitutes for the natural products named. These edible fats are artificial mixtures of different oils and fats, especially so the first three groups of edible fats that will be considered below.

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[1] A table oil consisting of a "blend" of several oils, such as arachis and olive oil, or cotton seed and olive oil, is not necessarily an adulterated oil.

From a sanitary point of view no objection can be raised against the substitution of the cheaper animal or vegetable fats for the more expensive animal or vegetable fats, as long as these substitutes are sold *under their proper name*, and *are not* used for fraudulent purposes. It is rather to be desired that the industry of fat substitutes should extend further, yielding, as it does, cheap palatable food-stuffs, and thereby tending to exclude from consumption the unwholesome fat from diseased animals, etc.

The quality of an edible fat, irrespective of the nature of its components, depends in a great measure on its palatableness. Some writers are of the opinion that an edible fat should be declared unsuitable for consumption if the free fatty acids exceed a certain percentage, but any such rule must appear an arbitrary one. Although the determination of the amount of free fatty acids should not be omitted, yet the valuation of an edible fat cannot be based on the amount of the free fatty acids it contains. Taste alone must decide whether the amount of free fatty acids is excessive.

The question as to digestibility of an edible fat hardly falls within the province of a chemist: still, it may be pointed out that *J. König*[1] takes objection to *A. Mayer's*[2] and *A. Jolles'*[3] statements that margarine is just as easily digested as butter fat, and that both fats have the same nutritive value. Although *König's* opinion is being contested by *Lührig*[4] on the strength of a physiological experiment, it has been shown by prolonged observations (*Leffmann*[5]) that substitution of butter in the diet by margarine resulted in a greatly diminished[6] consumption of fat as compared with the amount of butter taken previously, this being doubtless due to the less appetising properties of margarine.

I subdivide the edible fats into the following four groups :—

(1) Suet Substitutes.
(2) Butter Substitutes.
(3) Lard Substitutes.
(4) Cacao Butter Substitutes, Chocolate Fats.

To which I add the pharmaceutical oils and fats :—

(5) Effervescent Fats.
(6) Phosphorised Fats, Phosphorated Oils.

Another group of pharmaceutical oils and fats, falling under the heading of "Industries in which the Glycerides undergo a Chemical Change, but are not Saponified," will be described p. 962.

[1] *Die menschlichen Nahrungs. und Genussmittel*, 2nd ed. 2, 306.

[2] *Landw. Versuchs. Stat.* 29, 215.

[3] *Milch-Zeitung*, 1894, 670. "Ueber Margarine" (pamphlet), Bonn, 1895.

[4] *Zeit. f. Unters. Nahrungs. u. Genussm*, 1899, 484, 622, 769 ; 1900, 73.

[5] *Second Annual Report of the Dairy and Food Commissioner of Pennsylvania.*

[6] Cp. also R. Kayser, *Zeit. öffent. Chemie.* 1899, 101.

(1) SUET SUBSTITUTES

(German—*Praeparirter Talg*)

Artificial cooking fats are sold as substitutes for "suet" or "dripping." They consist of a mixture of suet (tallow) and cotton seed oil or cotton seed stearine. The consistence of these mixtures varies between that of tallow and lard, according to the proportion of added cotton seed stearine.

If it be necessary to ascertain the amount of cotton seed oil, the determination of the iodine value will give the readiest answer.

On the Continent a similar cooking fat is being sold under the name "Schmelzmargarine" (cp. "Schmelzbutter," p. 831), this being the fatty matter obtained on melting margarine and separating it from water after allowing to settle out (cp. also "Lard Substitutes," p. 926).

(2) BUTTER SUBSTITUTES

(*a*) **Margarine, "Oleomargarine"** [1]

French—*Margarine.* German—*Margarine.*
Italian—*Burro di margarina.*

The industry of butter substitutes owes its origin to experiments made by *Mège-Mouriès*, which were worked out to a manufacturing process in Paris during 1870.

The most important conditions to be observed in the margarine industry are the employment of the freshest and purest materials and the utmost cleanliness in all manufacturing operations.

The butter substitutes—margarine, "oleomargarine"[1] (older names partly suppressed by legislation are "butterine," "Dutch butter" [German—"*Kunstbutter*," "*Sparbutter*,"])—consist of a mixture of animal fats and vegetable oils and fats coloured yellow (unless forbidden by law), with annatto, methylorange, etc. The animal fats are oleomargarine—oleo oil—or neutral lard (the latter is almost exclusively used in the United States). Both ingredients must be prepared from the freshest beef fat or hog fat.

For the production of oleomargarine, the rough fat is removed from the slaughtered animal as quickly as possible and brought immediately into the works, where it is sorted. The kidney fat is selected and carefully washed with warm water and thoroughly cleaned. The cleaned fat is then brought immediately into large, well-aired, artificially cooled rooms to dry and harden (being allowed to hang there suspended from tin hooks for several hours), or is immersed into iced water in order to secure more rapid hardening.

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[1] This is the American term for our "margarine." The American equivalent of the term oleomargarine as used in this country is "oleo oil" or "margarine oil."

The hardened fat is then cut up and shredded in a shredding machine, and finally ground between rollers. The disintegrated mass is then immediately introduced into tin-lined, jacketed vessels (melting kettles), and brought to a temperature not exceeding 45° C., this temperature being maintained by steam or hot water passing through the jacket.

At this temperature only a portion of the fat contained in the tissue separates on the top of the comminuted rough fat. The settling and clearing is assisted by scattering salt over the surface of the melted fat. This melted portion, appropriately termed "premier jus," is run off into shallow, tin-lined trays arranged in tiers in a cooled room, when the bulk of the "stearine" separates out in a crystalline condition. The crystallised mass in the tins is cut up into square pieces of about 3 lbs. weight, wrapped in canvas cloths, and placed into hydraulic presses.

For the best qualities of margarine, the "premier jus" is remelted and allowed once more to settle out, after salt has been added, whereby the last traces of membrane and tissue are precipitated. In large works the clear fat is then allowed to run into wooden vats, in which it stands for three to five days at a temperature suitable for the crystallisation of the "stearine." The whole is then stirred up into a homogeneous pulpy mass; this is wheeled to the presses and packed into them in small pieces wrapped in canvas cloth, weighing about 3 lbs. each.

The oleomargarine, "oleo-oil," which runs out from the presses forms the chief raw material for the manufacture of margarine.

Amongst the vegetable oils, cotton seed oil and cotton seed stearine take the most prominent place. According to the intended quality of the margarine the quality of the cotton seed oil varies. In any case the cotton seed oil must be practically devoid of free fatty acids, and rendered as free as possible from the peculiar flavour characteristic of this oil. The best brand of cotton seed oil used for margarine making is known under the name "butter oil." Arachis oil (also olive oil) and sesamé oil are used to a greater extent in Europe than in the United States. Latterly also refined cocoa nut oil (see (β)) is being introduced into margarine.

The oleomargarine, "oleo oil," is mixed in churning machines with the vegetable oils and fats and with milk. Hence the milk department forms a substantial portion of a margarine works. Previous to being mixed with the fatty matter, the milk must be "pasteurised." As a rule, the cream has been taken off before the milk reaches the margarine works. Otherwise it is removed by means of a centrifugal machine.

The churning machines consist of oval jacketed vessels provided with one or two sets of stirring and mixing gear. During the process of churning a constant temperature is maintained by means of steam sent through the jacket of the churn.

The object of churning, besides thoroughly mixing the ingredients, is to destroy the tendency of the oleomargarine to crystallise, and by pulverising the mixture into single globules, such as butter fat forms in milk, to produce a thorough emulsion. The steam is then turned off and the warm material is cooled by cold water sent through the jacket.

From the churn the cooled margarine is run into cooling tanks, which are built up of marble or tiles or simply consist of large wooden tanks. Whilst running out, the margarine is met by a current of ice-cold water, delivered under high pressure, in order to thoroughly pulverise the margarine, so that the disintegrated globules, after solidifying, somewhat resemble butter granules.

The solidified margarine is taken out of the cooling cisterns by means of long wooden spoons, placed in wooden waggons where admixed water drains off, and then carted to large kneading machines.

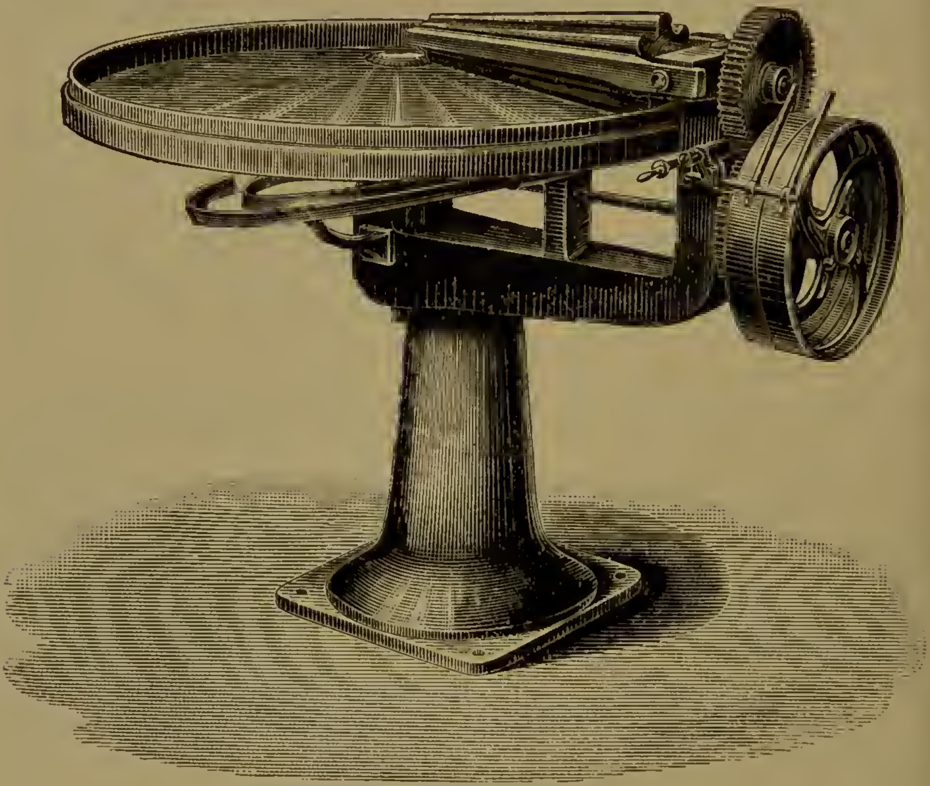

Fig. 62.

These consist of huge, circular, wooden tables (Fig. 62), which rotate slowly, whilst at the same time a set of conical, fluted, or specially shaped rollers move along the top of the revolving tables. The margarine is thus thoroughly worked through, and the excess of water squeezed out, so that a homogeneous mass results. This is then salted to taste, mixed with a little colouring matter, and again submitted to thorough kneading, in order to produce the required texture throughout the whole mass. The margarine is finally moulded into lumps, pats, rolls, or any other desired shape.

A general working recipe for the manufacture of margarine is the following:—Mix 65 parts of oleomargarine, 20 parts of vegetable oils, and 30 parts of milk. The yield is 100 parts of finished product, 15 parts of water being eliminated in the course of manufacture.

In the following tables are given, by way of examples, the components of three grades of margarine as manufactured in the United States:[1]—

High Grade Margarine

Oleomargarine, "Oleo oil"	100	parts
Neutral lard	130	,,
Butter	95	,,
Salt	32	,,
Colouring matter	0·5	,,
	357·5	parts

yielding about 352 parts of "oleomargarine."

Medium High Grade Margarine

Oleomargarine, "oleo oil"	315	parts
Neutral lard	500	,,
Cream	280	,,
Milk	280	,,
Salt	120	,,
Colouring matter	1·5	,,
	1496·5	parts

yielding from 1350 to 1380 parts of "oleomargarine."

Cheap Grade Margarine

Oleo oil	495	parts
Neutral lard	265	,,
Cotton seed oil	315	,,
Milk	255	,,
Salt	120	,,
Colouring matter	1·25	,,
	1451·25	parts

yielding from 1265 to 1300 parts of "oleomargarine."

For still lower qualities maize oil is used in the United States, but owing to the very pronounced flavour this oil possesses, it can only be employed for the lowest brands of margarine, as it is extremely difficult to remove or to mask the peculiar grainy flavour of maize oil. In Europe lard is little used. In this country oleomargarine is prepared exclusively from beef fat. Mutton fat, which imparts an unpleasant ("animal") flavour to the margarine, is,

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[1] *Census Bulletin.*

however, used in continental margarine factories. In Russia sunflower oil is used in the manufacture of margarine, and mixtures of this oil with cocoa nut oil, butter, and oleomargarine are largely substituted for genuine butter.

The object of the margarine maker being to render his product as closely similar to butter as possible, and to take away the tallowy or too strongly fatty taste of the material, some manufacturers (provided the law permits) add butter (cp. the above-given tables). Others add small quantities of volatile acids,[1] volatile aldehydes,[2] mixed glycerides containing butyric acid, such as dibutyromonostearin and dicaprylomonostearin,[3] or "butter perfumes" which consist chiefly of volatile acids, such as propionic, butyric, caproic. An important point in the manufacture is to produce margarine which will froth[4] and "brown" on heating, so that even in cooking the margarine may resemble butter. Since the property of butter to brown and froth is due to caseïn and milk sugar, it is evident that the more milk used in the manufacture of margarine the nearer will the product approximate to butter. This is done largely in this country and in America, but in some continental countries (see below) where the law forbids the addition of more than a strictly limited quantity of milk, a number of patents have been taken out[5] for substances which are credited with imparting to margarine the desired properties. Prominent amongst these patented products are caseïn and other albuminoids.[6] Others add cholesterol and cholesteryl esters,[7] or lecithin.[8] Vegetable waxes have also been proposed as admixtures, and the use of beeswax[9] for this purpose has even been patented, although the addition of these substances must reduce the digestibility of the margarine.

The manufacture of butter substitutes is differently affected by legislation in different countries.[10] In this country the mixing of margarine with butter in any proportion was at first allowed, as, according to the Margarine Act of 1887, any "butter" containing even the smallest quantity of foreign fat is looked upon as margarine. By the Margarine Clause of the Food and Drugs Act, 1899, however, the maximum proportion of butter fat in margarine has been restricted to 10 per cent.

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[1] Eng. Pat. 1898, 15,535 (Wohlgemuth); Eng. Pat. 1900, 15,649, 22,458; Germ. Pat. 121,657 (Poppe).

[2] Germ. Pat. 135,081 (Neudörfer and Klimont).

[3] Germ. Pat. 107,870.

[4] According to Pollatschek. *Chem. Revue*, 1904, 27, the frothing is due to soap (!?).

[5] Cp. Germ. Pat. 112,687, 113,382, 116,792.

[6] Under the name "Vitello," a mixture of egg yolk and glucose has been patented, and is stated to be largely used in Holland, Bernegau, Germ. Pat. 97.057. Cp. also Germ. Pat. 113,382 (Evers), and Eng. Pat. 1900, 21,626 (Neisse and Boll).

[7] Sprinz, Eng. Pat. 1901, 7620; Germ. Pat. 127,376.

[8] Germ. Pat. 142,397.

[9] Eng. Pat. 1900, 22,905; Germ. Pat. 124,410.

[10] A. Lavalle, *Die Margarine Gesetzgebung*, Bremen, 1896; *Report of the Departmental Committee on Butter*, Eyre and Spottiswoode, 1904.

In the United States the mixing of butter with margarine is not forbidden, provided this product be sold as "oleomargarine." In France also the admixture of butter with margarine is permitted, provided the article so prepared is sold with a proper declaration as to the composition. In Germany, on the contrary, as also in Austria, the mixing of margarine with butter is prohibited both in the course of manufacture and as an addition to the finished margarine. Since in the manufacture of margarine no more than 100 parts of milk or a corresponding quantity of cream may be used for 100 parts of foreign fats, the German and Austrian margarines may therefore not contain more than 3·5 per cent of butter fat in the melted fat; hence the *Reichert-Meissl* values of the German and Austrian margarines must not exceed the figure 2. (If cocoa nut or palm nut oil has been used, the *Reichert-Meissl* value will be higher; see below.)

By an Imperial Statute it is made obligatory on the part of the margarine manufacturers in Germany to add at least 10 parts of sesamé oil for every 100 parts of fats and oils used. This is done in order to facilitate the detection of margarine in butter (earlier proposals to add a "latent" colouring matter, such as phenolphthalein or dimethylamidoazobenzene, having been rejected).

In Austria the addition of 10 per cent of sesamé oil has also been made obligatory. In Belgium the margarine manufacturer is bound to use at least 5 parts of sesamé oil in 100 parts of fatty matter, and 1 part of potato starch. In Denmark the proportion of butter fat allowed in margarine has been reduced from 50 per cent to 12 per cent.

The examination of margarine ("oleomargarine"), and especially the methods of distinguishing it from true butter fat, have been exhaustively dealt with in the preceding chapter, under "Butter Fat."

A reliable preliminary test for discriminating margarine not containing any butter from genuine butter fat, is to heat the fat with alcoholic potash in such a quantity that the fat is not saponified completely (*Hehner*[1]). In the presence of butter fat the formation of ethyl butyrate, which is readily recognised by its pleasant smell recalling that of pine-apples, will indicate the presence of butter. A number of margarines examined by the writer failed to give the odour of the butyrate. On adding, however, a small quantity of genuine butter, the odour appeared immediately.

In order to determine quantitatively the amount of butter fat in margarine, especially with a view to testing whether it exceeds the legal limit of 10 per cent, the *Reichert-Wollny* method has been agreed upon as the official test by the Government Laboratory and a Committee of the Council of the Society of Public Analysts. The following table gives the amount of butter fat which is assumed to be present in a margarine in case the following *Reichert-Wollny* numbers have been found :—

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[1] *Analyst*, 1884, 76.

Reichert-Wollny Number of the Margarine Fat.	Percentage of Butter Fat assumed to be present in the Margarine Fat.
4·0	10
4·3	11
4·6	12
4·9	13
5·2	14
5·5	15
5·9	16
6·2	17
6·5	18
6·8	19
7·1	20

Since margarines are now prepared which contain as much as 30-40 per cent of cocoa nut or palm nut oil, indications furnished by the *Reichert-Wollny* value alone are not sufficient to raise the presumption that the margarine contains more butter fat than is permitted under the Foods and Drugs Act. In cases of this kind, however, the high saponification number of the margarine fat will readily reveal the presence of cocoa nut or palm nut oil.

In conclusion I add a few analyses of margarines, which indicate the course of examination. This embraces the determination of water (which should not exceed 10-12 per cent), ash, total fat, and examination of fat (if desired).

Composition of some Margarines free from Cocoa Nut Oil

	Water.	Fat.	Solids. Not-Fat.	Ash.	NaCl.	Saponification Value.	Iodine Value.	Reichert Value.	Hehner Value.	Butyro-refractometer. At 45° C.	Observer.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Mgrms. KOH.	Per cent.	c.c. $\frac{1}{10}$ norm. KOH.	Per cent.	" Degrees.	
Margarine 1 . .	8·8	88·78	2·33	1·58	1·53	...	...	0·33	94·5	...	Partheil[1]
,, 2 . .	8·5	88·81	2·69	1·6	1·74	...	...	0·44	94	43·2	,,
,, 3 . .	8·6	88·9	2·4	1·6	1·5	...	...	1·43	94·7	...	,,
,, 4 . .	...	...	...	...	...	193·70	...	2·07	...	...	Beythien and Strauss[2]
,, 5 . .	...	...	..	...	...	194·00	53·60	1·44	96·30	...	
,, 6 . .	...	...	...	...	...	200·60	...	1·78	...	...	,,
,, 7 . .	...	...	...	...	...	203·75	...	1·93	...	...	,,
,, 8 . .	...	...	...	...	...	195·00	60·90	2·40	95·88	...	,,
,, 9 . .	...	...	...	...	...	196·05	...	1·19	...	...	,,
,, 10 . .	...	...	...	...	...	199·80	52·12	1·52	95·50	...	,,

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[1] *Apoth. Zeitung.*, 12, 220.

[2] *Zeit. Unters. Nahrungs. und Genussm.* 1902, 856.

The examination of a few specimens of fat from margarine, containing cocoa nut oil, gave the following numbers :—

Margarine Fats containing Cocoa Nut Oil

Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Hehner Value.	Observer.
216·34	49·46	5·50	92·97	Beythien and Strauss
220·35	49·06	4·50	93·04	
217·45	...	4·50	...	,,
210·12	...	4·10	...	,,
218·24	49·25	4·60	92·98	,,

The detection of the individual oils and fats in margarine is carried out in the manner described under "Butter Fat." In an examination of this kind, the determination of stearic acid may lead to valuable indications, as evidenced by the following numbers published by *Hehner* and *Mitchell* :—

Fat.	Containing Stearic Acid. Per cent.
Oleomargarine	21·3-23·6
Margarine I.	24·8
,, II.	11·72

Butter fat contains less than 1 per cent of stearic acid (cp. p. 405).

The analysis of a margarine fat of the iodine value 69·49 by the lithium salt method gave the following results (*Partheil* and *Ferié*) :—

Stearic acid	19·14 per cent
Palmitic acid	6·08 ,,
Myristic acid	14·33 ,,
Lauric acid	7·04 ,,
Unsaturated acids (of which 20·3 per cent are stated to be less saturated than oleic)	47·06 ,,
	93·65 ,,

Leffmann and also *Geisler*[1] stated that they found in "oleomargarines" from 9·72-11·5 per cent of paraffin wax; hence the determination of the unsaponifiable matter should not be omitted. As regards the examination for boric acid and colouring matter, see p. 828, under "Butter Fat." For the detection of egg yolk a method has been worked out by *Fendler*.[2]

In the following table I give the estimated production of margarine in the most important countries during the year 1900 :[3]—

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[1] *Journ. Amer. Chem. Soc.* 1899 (21), 605.

[2] *Ber. d. deutsch. pharm. Ges.* 1903, 284.

[3] *Census Bulletin.*

Estimated Production of Margarine during 1900

	Pounds.
Germany	220,000,000
Netherlands	123,000,000
United States, more than	100,000,000
United Kingdom	82,000,000
Denmark	35,000,000
Sweden	22,000,000
Norway	22,000,000
Belgium	20,000,000

The following table[1] shows the quantities and kinds of materials used in the production of "oleomargarine" in the United States for the (fiscal) year ended 20th June 1899:—

Materials.	Pounds.	Percentage.
Neutral lard	31,297,251	34·27
"Oleo oil"	24,491,769	26·82
Cotton seed oil	4,357,514	4·77
Sesamé oil	486,310	0·53
Colouring matter	148,970	0·16
Sugar	110,164	0·12
Glycerin	8,963	0·01
"Stearine"	5,890	0·007
Glucose	2,550	0·003
Milk	14,200,576	15·55
Salt	6,772,670	7·42
"Butter oil"[2]	4,342,904	4·76
Butter	1,568,319	1·72
Cream	3,527,410	3·86
Total	91,322,260	100·00

(β) Vegetable Butters

A butter substitute made from cocoa nut oil or palm nut oil was originally prepared for the Indian market, where the native population are forbidden by their religious tenets to consume beef fat or hog fat. This vegetable butter has recently found extensive use at home in confectionery and as a cooking fat. It is being sold under a variety of fancy names, such as "lactine," "vegetaline," "cocoaline," "laureol," "nucoline," "albene," "palmine," "cocose," "kunerol," etc.

This vegetable butter is prepared from the best brands of cocoa nut oil (Cochin), or expressed palm kernel oil. The free fatty acids are removed by various processes, such as by treatment with alcohol to dissolve out the free fatty acids and subsequent filtering over animal charcoal (*Schlinck*[3]), or by neutralising the free fatty acids by

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[1] Chandler, *Journ. Soc. Chem. Ind.* 1900, 619.

[2] This is a special brand of cotton seed oil (see p. 529).

[3] United States Patent, 653,041.

means of magnesia (*Jeserich*[1]) or lime (*Ruffin*[2]), etc. Vegetable butter is therefore practically neutral cocoa nut or palm kernel oil, or a mixture of both. This vegetable butter forms the raw material for the production of "chocolate fats" (see below).

Another kind of vegetable butter consists practically of cotton seed stearine; it is sold under such names as "vegaline," "cottolene."

(3) LARD SUBSTITUTES

German—*Kunstspeisefett*, *Kunstschmalz*.

The lard substitutes consist chiefly of a mixture of lard, or lard "stearine," with beef "stearine"[3] (American term, "oleostearine"), cotton seed stearine, cotton seed oil, maize oil, arachis oil, sesamé oil, cocoa nut oil, and palm kernel oil. In the infancy of this industry these artificial products were sold under such names as refined lard, etc. (cp. p. 783), and were frequently found to contain no lard whatever, being judiciously prepared mixtures of beef stearine and cotton seed oil, such as described above under (*a*). At present, however, all lard substitutes contain lard, or at least lard "stearine," as a basis. The manufacture consists simply in mixing the various fats and oils in the melted state in a churning machine and cooling the mixture rapidly by running it over cooling cylinders (cp. "Lard").

The examination of these substitutes is carried out on the lines indicated fully under "Lard" (chap. xiv. p. 794).

The examination of the unsaponifiable matter should not be omitted, since even patents have been taken out for lard substitutes containing mineral oils.

In some German works the lard substitutes are treated with onions and condiments so as to impart to these fats the taste of a cooking fat, and are sold under the name "Bratenfett" ("culinary fat," "dripping").

(4) CACAO BUTTER SUBSTITUTES—CHOCOLATE FATS

The natural chocolate fat is cacao butter (p. 794). Since more cacao butter is obtained from the cacao beans than is required for properly made chocolate, there is a surplus of cacao butter which is worked up for cheaper kinds of chocolate. Cacao butter being one of the most expensive fats, the demand for cheap substitutes has arisen. Animal fats are unsuitable for chocolate manufacture, as they are apt to impart an unpleasant flavour ("animal flavour") to the chocolate unless they are refined carefully. Hence chocolate fat substitutes are mostly prepared from vegetable fats. The chocolate fat substitutes in vogue at present are obtained from cocoa nut oil or palm kernel oil, refined as described under (*β*) "Vegetable Butters."

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[1] Jeserich und Meinert-Bünau, German Patent, 19,819.

[2] German Patent, 90,521.

[3] On the Continent also mutton stearine is used.

The original oils being too soft (*i.e.* of too low a melting point), the "stearines" from cocoa nut oil and palm kernel oil are prepared by melting the refined cocoa nut oil and palm kernel oil, and allowing to cool down to a suitable temperature so that the glycerides of the solid fatty acids crystallise out. The partly solidified mass is then expressed in hydraulic presses much in the same fashion as the "premier jus" is treated (p. 917) to remove the cocoa nut or palm kernel "oleine." According to the length of time during which the crystallised mass is allowed to stand under pressure, and according to the pressure employed, the melting point of the cocoa nut or palm kernel stearine varies. The melting points of a few of such products are given on p. 177. The physical and chemical characteristics have been tabulated, p. 751.

Since the melting points of the commercial cocoa nut "stearines" (sold under fancy names, such as "cacaoline," "cocoline," etc.) are still somewhat too low for the purposes of the chocolate manufacturer, they in their turn are being "stiffened," *i.e.* adulterated with small quantities of animal fats. It has even been stated that Japan wax[1] has been admixed to raise the melting point. Mineral waxes, like paraffin wax, ceresin, ought to be excluded, since they are indigestible.

The examination of these products embraces the determination of the melting point, and the detection of unsaponifiable matter and animal fats.

The preparation of suitable chocolate fats from vegetable fats of a higher melting point than cocoa nut oil or palm nut oil naturally suggests itself. Some of the tropical vegetable fats, such as margosa oil, mowrah seed oil, etc., may lend themselves for this purpose (*Lewkowitsch*).[2]

(5) EFFERVESCENT FATS

German—*Brausende Fette*

Under the heading of edible fats would also seem to fall those fats that are used for medicinal purposes. A type of these oils is the effervescent cod liver oil prepared by impregnating cod liver oil with carbonic acid, in order to render the oil more palatable.[3] Since these oils are saturated with carbonic acid under pressure, they effervesce as soon as the pressure is released.

(6) PHOSPHORISED FATS

German—*Phosphoroele*

These oils are prepared by dissolving phosphorus in oils and fats in the absence of air. They contain a small quantity of phosphorus

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[1] Possetto, *Giorn. Farm. Chim.* 1901 (51), 337.

[2] Cantor Lectures on "Oils and Fats: their Uses and Applications," *Journ. Soc. Arts*, 1904.

[3] Chemische Fabrik Helfenberg, German Patent, 1899, 109,446; J. Barclay, English Patent, 1902, 11,410.

only. *Katz*[1] has shown that the methods given above for the determination of phosphorus (p. 157) are not exact enough, and that the method proposed recently by *Straub*[2] (treatment of the phosphorised oil with an excess of a 5 per cent solution of copper sulphate, whereby a black copper phosphide is formed which is oxidised by persistent shaking with air so that the phosphoric acid may be determined in the solution by means of molybdate in the usual manner) suffers from several inconveniences. The method proposed by *Katz*[1] is the following:—10 grms. of phosphorised oil are agitated in a separating funnel with 20 c.c. of a 5 per cent aqueous copper nitrate solution until a permanent black emulsion is produced, due to the formation of a copper phosphide (of the formula Cu_2P_2). 50 c.c. of ether are then added, and 10 c.c. of hydrogen peroxide solution are entered in small portions until the black emulsion is completely discolourised. The aqueous layer is then run off, the ethereal layer is shaken out three times successively with 10 to 20 c.c. of water, the united aqueous solutions are acidulated with a few drops of hydrochloric acid and evaporated to 10 or 20 c.c. on the water bath. If required, the acid liquid is filtered and sufficient ammonia is added to re-dissolve the precipitate first formed. The phosphoric acid is then precipitated in the usual manner with magnesia mixture.

In case the hydrogen peroxide employed contain phosphoric acid (usually added to render it more stable), the amount of the acid must be ascertained in a blank test.

If the amount of oxidised phosphorus in a phosphorised oil be required, the oil must be first extracted with water which has been saturated with carbon dioxide. The phosphorus is determined both in the aqueous extract and in the phosphorised oil.

Katz prepared a number of phosphorised oils by placing dried phosphorus with oil in a bottle containing an atmosphere of carbon dioxide, warming the contents slowly in a water bath until the phosphorus had melted, and shaking the mixtures (in a shaking machine) for one to two hours. The amounts of phosphorus dissolved were determined by the above described method. The following results were obtained:—

Phosphorised Oil from	Phosphorus. Per cent.
Linseed Oil	1·15
Poppyseed Oil	1·10
Sesamé Oil	1·06
Rape Oil	1·16
Almond Oil	1·13
Arachis Oil	1·20
Olive Oil	1·085
Castor Oil	0·70
Cod Liver Oil	1·13

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[1] *Archiv d. Pharm.* 1904, 121.

[2] *Ibid.* 1903; cp. also *Zeit. f. anorg. Chem.* 1903. 460.

II. BURNING OILS

French—*Huiles d'eclairage.* German—*Brennoele, Leuchtoele.*
Italian—*Olii da lumi*

Although the expansion of the mineral oil industry has caused a great reduction in the amount of fatty oils used for illumination, their employment is still considerable. Enormous quantities of rape oil are used on the railways in this country, of lard oil in the United States, and of olive oil in Italy. The best brands of seal oil and whale oil are employed as illuminants in lighthouses; whale oil is also used in Norway for lighting the streets, etc.

The preparation of these oils has been described in the foregoing chapter. Their examination comprises tests for purity and the determination of free fatty acids. The former include mucilaginous substances or other impurities, the presence of which is due to defective refining. These rise in the wick with the oil and are apt to clog it up, so that carbon is deposited, and the flame becomes smoky. Since drying and semi-drying oils are unsuitable burning oils, their absence must be ascertained by the methods given in the foregoing chapter.

The importance of these tests to large consumers may be gathered from the fact that lard oil adulterated with 25 per cent of cotton seed oil will not burn for longer than six to eight hours without clogging the wick, whereas pure lard oil will burn as long as twelve to fourteen hours. (Small consumers hardly note such drawbacks, and it is, therefore, easily explained why cotton seed oil, and even linseed oil (in India), and tung oil (in Japan), are used as burning oils.[1])

The determination of the free fatty acids is also important, since oils containing more than 5 per cent of free fatty acids are unsuitable burning oils, as they cause charring of the wick. Since rape oil is refined by means of sulphuric acid, burning oils should also be tested for mineral acids by shaking out a somewhat large quantity of the oil with warm water and examining the aqueous solution (cp. IV., "Lubricating Oils").

III. PAINT OILS

French—*Huiles siccatives.* German—*Maleroele.*

Under the term "paint oils" are comprised those vegetable oils which are used as vehicles for applying pigments to the surface of bodies, either as a preservative or for decorative purposes. Only the vegetable drying oils are useful; the paint oil *par excellence* is linseed oil. In the manufacture of high-class white paints for the use of artists, walnut oil and poppy seed oil are employed in considerable quantities. The semi-drying oils, such as cotton seed oil or maize oil, are unsuitable as paint oils.

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[1] In the Tibetan lamasseries butter fat is used as a burning oil.

The examination of these oils chiefly embraces tests for purity. The detection of adulterants, such as mineral oils, rosin oils, and fish oils, have been fully described under the heading of linseed oil, etc. Fish oils, especially menhaden oil, were used in considerable quantities to adulterate linseed oil when the price of the latter was high, and a large number of linseed oil substitutes, consisting of linseed oil adulterated with fish oil, mineral oils, and chiefly rosin oils, were then placed on the market.

If the oil in a ready mixed paint has to be determined quantitatively, the oil must be separated from the pigment by extraction with ether. The examination of the oil itself is carried out by the methods detailed in the foregoing chapters.

In judging of the value of a drying oil for mixing with paints, the effect of the pigment with which it is to be ground must not be lost sight of, inasmuch as some pigments greatly facilitate the drying, whereas others so much retard it that driers must necessarily be added.[1]

It should be noted that oils extracted by solvents are not suitable as paint oils.

Since paints for common use are chiefly prepared with "boiled oils," the reader must be referred for further information to the section on "Boiled Oils" (p. 969).

IV. LUBRICATING OILS—LUBRICANTS

French—*Huiles lubrifiantes.* German—*Schmieroele, Schmiermittel.* Italian—*Olii lubrifianti.*

Before the advent of the industry of lubricating oils from mineral oils, especially those prepared from petroleum, the lubricating oils in use were almost exclusively represented by fatty oils, solid fats, and liquid waxes. Hence the examination of lubricating oils formed a distinct province of fat analysis. Within the last decades the mineral oil industries have made striking advances, so that the mineral oils have greatly restricted the employment of fatty oils for lubricating purposes. Still, large quantities of fatty oils are used nowadays, especially in admixture with mineral oils. Hence also mineral oils, and mixtures of fatty oils with mineral oils, must be considered here briefly.

The solid lubricating greases also fall within the purview of fat analysis, and will therefore be dealt with at the end of this section.

Owing to the great technical importance of this subject, a number of works have been published, treating solely of the lubricating oils and lubricants. Here only a concise survey of the subject can be given, and those requiring special information must be referred to the

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[1] Cp. Lotter, *Chemiker Zeitung*, 1894, 1696.

works given in the footnote.[1] I subdivide the lubricants into four groups:—

1. FATS (FATTY OILS AND SOLID FATS) AND LIQUID WAXES.
2. MINERAL OILS.
3. BLENDED OILS (MIXTURES OF GROUPS (1) AND (2)).
4. SOLID LUBRICANTS, GREASES.

1. FATTY OILS AND LIQUID WAXES

The most important fatty oils used are tallow oil, lard oil, neat's foot oil, olive oil, rape oil, and castor oil. Also tallow itself is still largely used. For delicate machinery hazel nut oil, ben oil, porpoise oil, and dolphin oil (black fish oil) have come in vogue. Cocoa nut oil is not a suitable lubricant.

The vegetable drying oils, semi-drying oils, fish oils, and blubber[2] oils are not suitable for lubricating purposes; hence their admixture with the above-named lubricating oils constitutes adulteration.

The liquid waxes, sperm oil and Arctic sperm oil, are excellent lubricants, and are almost exclusively used in their pure state for the lubrication of light machinery and spindles. The manufacture of these oils and the refining processes have been described under the heading of each oil in the foregoing chapter, where also the methods of examining for adulterants will be found. The amount of unsaponifiable matter in the vegetable and animal oils should be small. The liquid waxes yield, of course, considerable quantities of alcohols, which are comprised in practice under the name "unsaponifiable matter."

2. MINERAL OILS

The mineral oils used for lubricating purposes are derived from crude petroleum, shale, and lignite. They are represented by hydrocarbons (saturated, unsaturated, closed-chain hydrocarbons) boiling above 300° C. Their specific gravities lie above 0·840. Those of a specific gravity up to 0·900 are almost exclusively products of distillation. The mineral oils derived from petroleum are obtained by distilling the crude petroleums. Shale oils and lignite oils are the distillation products of the tar obtained on destructively distilling the shale and lignite respectively.

Mineral lubricating oils of a specific gravity exceeding 0·910, are either "concentrated" ("reduced") oils, or distilled oils. The former are obtained by distilling off the lower boiling hydrocarbons

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[1] Grossmann, *Die Schmiermittel;* Wiesbaden, 1894. Carpenter-Leask, *Soaps and Candles*, chap. xii. written by J. Veitch Wilson. Holde, *Die Untersuchung der Schmiermittel;* Berlin, 1897. Archbutt and Deeley, *Lubrication and Lubricants;* London, 1900.

[2] With the exception of porpoise and dolphin oils.

from petroleum until a still residue of such a concentration remains behind, that after refining by filtration, etc., it is suitable for lubricating purposes. The distilled oils are prepared by distilling the residues obtained after removing the lower boiling hydrocarbons in a current of steam in a vacuum, so as to prevent "cracking." Distilled oils containing products of destructive distillation are unsuitable for lubricating purposes. Details of the manufacture of these oils fall outside the scope of this treatise.

3. BLENDED OILS

Mineral oils being miscible with all fatty oils—excepting castor oil—and liquid waxes, extensive use is made of this miscibility in practice, and a great number of commercial lubricating oils consist of such mixtures. Castor oil can be made miscible to a certain extent with mineral oils by mixing it first with a fatty oil such as tallow oil. The miscibility of castor oil with lubricating oils, as determined by *Archbutt*,[1] is given in the following table:—

Miscibility of Castor Oil with Mineral Oils

Mineral Oil.	Specific Gravity at 15·5° C.	c.c. of Mineral Oil miscible with 10 c.c. of Castor Oil at 59° F.
Scottish shale .	0·865	3·7
,, ,, . .	0·890	2·45
American . .	0·907-0·912	1·7

"Blown oils" (cp. p. 981) also are largely mixed with mineral oils or with blends of mineral oils and fatty oils.

4. SOLID LUBRICANTS, GREASES

This class of lubricants is prepared from a great variety of fatty oils, solid fats, mineral oils, rosin oils, alkali metal soaps of fatty acids or rosin acids, and of lime soaps and aluminium soaps of fatty acids or rosin acids. In some cases water is introduced together with the soaps. Other greases are mixed with weighting substances, or with talcum or plumbago.

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[1] Archbutt and Deeley, *Lubrication and Lubricants*, p. 110.

EXAMINATION AND VALUATION OF LUBRICATING OILS

The valuation of the lubricating oils described under [1], [2], and [3] is carried out by means of *physical*, *chemical*, and *mechanical* methods.

Physical Tests

The physical methods comprise the determination of (1) the specific gravity (p. 159), (2) the viscosity (p. 197), and (3) the freezing point (p. 183).

With regard to the **specific gravity** it may again be pointed out that it affords little or no information as regards the lubricating power of an oil. The specific gravity number is, however, useful in determining the kind of work for which a lubricating oil is suitable, or as a test of identity, and further, to direct attention to adulteration with rosin oils or tar oils (cp. chap. ix. p. 382).

The **viscosity** does not furnish an absolute means of determining the lubricating value of an oil, although it enables us to draw certain conclusions. Thus, if the viscosity is low, the film of oil which keeps the bearings of rapidly moving machinery apart is not so fully formed that the metal surfaces are kept asunder, and therefore the friction between them is not sufficiently diminished. Again, if the viscosity of an oil be too high, the resistance of the film is so great that heating occurs, and the bearings become warm, or even hot, the heat so generated being proportional to the internal friction of the oil, or in other words, to its viscosity. That oil will prove the best which under given conditions of speed, pressure, and temperature, has the lowest permissible viscosity.

Petroff[1] measures the internal friction of oils, *i.e.* the absolute viscosity. More recently *Archbutt* and *Deeley*[2] have determined the absolute viscosities[3] of water and glycerin solution. Since, however, the viscosity, expressed in terms of absolute viscosity, is not likely to replace in the immediate future the usual manner of expressing viscosity; furthermore, since it would follow from *Petroff's* observations that at a given temperature the order of the oils with respect to their internal frictions is the same as their lubricating power and their viscosity as ascertained in the usual manner, I must refer the reader for further information on absolute viscosity to *Archbutt* and *Deeley's* work.

If it is desired to examine the unsaponifiable portion of a blended oil viscosimetrically, the viscosimeters described in Chapter V. will, as a rule, be found too large. *Künkler's* viscosimeter, requiring only 30 c.c., may be found useful in such cases.

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[1] Grossmann, *Die Schmiermittel*, pp. 42-49.

[2] Archbutt and Deeley, *Lubrication and Lubricants*, p. 126.

[3] Cp. also Chenevier, *Moniteur Scient.* 1898, 785.

Kunkler's[1] viscosimeter (Fig. 63) consists of a sheet brass (oil- or) water-bath, *w*, provided with a copper bottom, the contents of which may be heated by a gas burner; the temperature of the heating liquid is read off a thermometer held by *x*; *w* contains the removable stand *d* placed firmly on four legs, and supported by two brackets *h*. In this stand fits the viscosimeter, made of strong glass and consisting of the charging-funnel *k*, the bulb *e* bearing the mark *f*, the capillary tube *c*, the lower bulb *a*, and the ascending tube *b*; the whole apparatus is held in position by the spring-clamp *i*. The temperature of the contents of the viscosimeter is controlled by a thermometer fixed in *k*. The ascending tube *b* is supported by *l*; it is fitted with a tap, *m*, and connected by means of india-rubber tubing with the suction apparatus *r*, in which the mercury used for aspirating the oil is allowed to rise up to the mark *p*. Bulb *t* serves as a receptacle for the mercury; the can *y* is used for warming the oil to the desired temperature.

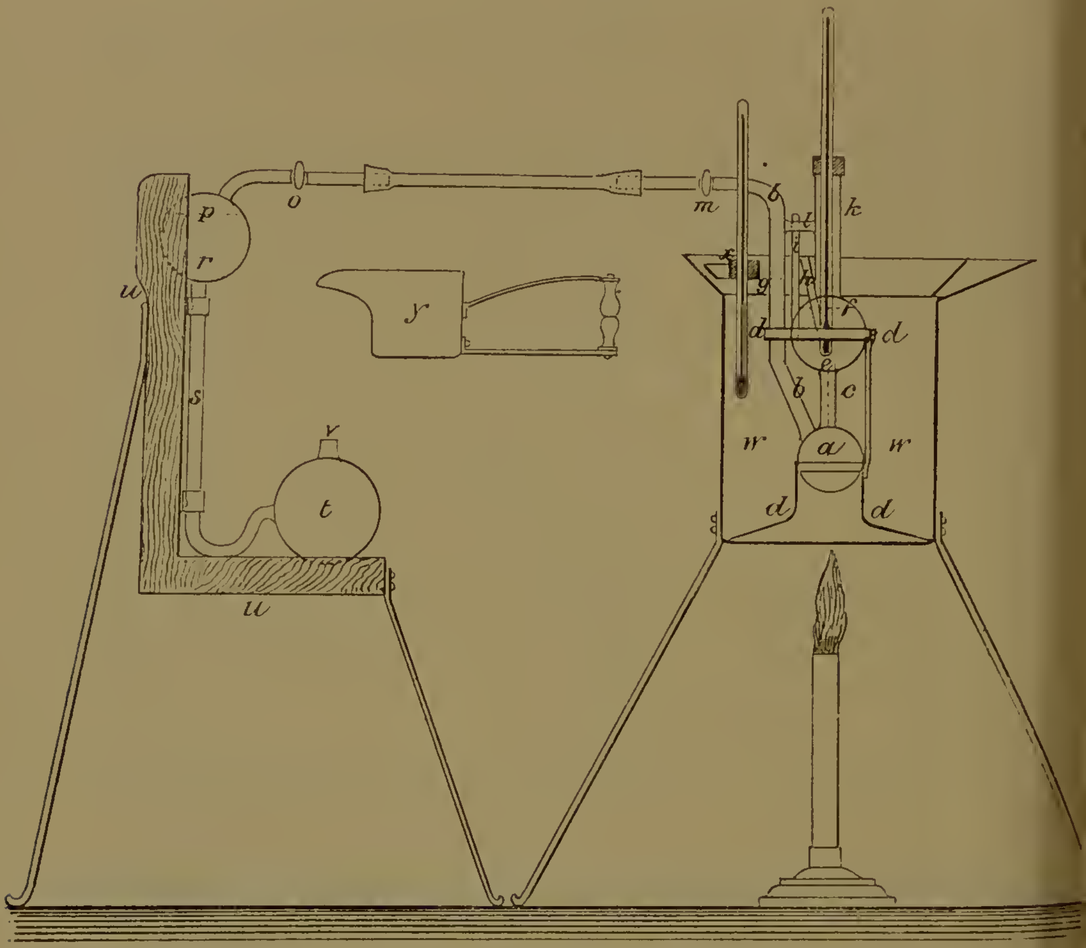

Fig. 63.

The apparatus is gauged with a dilute glycerin solution of 1·110 specific gravity at 20° C.; the time required for its outflow

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[1] *Dingl. Polyt. Journ.* 290. 281.

at 20° C. is taken as unity. For temperatures up to 100° C. mercury is used as the aspirating liquid; for higher temperatures water is preferred. The heating vessel *w* is filled with water for temperatures up to 100° C.; for temperatures above 100° C. a mineral oil of suitable boiling point is used.

The test is carried out in the following manner:—Fill *r* up to the mark *p* with the aspirating liquid and heat the bath. In the meantime warm the oil to be tested in the can *y* a few degrees above the required temperature. Take the viscosimeter for a short time—say half a minute—out of the bath so that the air in *a* is somewhat cooled, and then put it back, filling at the same time vessel *e* with the oil up to mark *f*. The air in *a* will then expand so that no oil can enter. Allow the oil in *e* to assume the temperature of the bath, connect the viscosimeter with the aspirator, and open tap *o*. Then open tap *m* and observe accurately the time required by the oil to rise in the ascending tube *b* up to the mark *g*.

For the accurate dimensions of the various parts of the apparatus (made by *C. Desaga* of Heidelberg), the original paper must be consulted.

The following table contains a few viscosimetric constants determined with this apparatus, contrasted with the numbers obtained by means of *Engler's* viscosimeter:—

Kind of Oil.	Künkler's Viscosimeter.						Engler's Viscosimeter.					
	Seconds at			Glycerin Solution, Spec. Grav. 1·110 at 20° C. (66 seconds) = 1.			Seconds at			Water at 20° C. (54 seconds) = 1.		
	°C.			°C.			°C.			°C.		
	20	50	150	20	50	150	20	50	150	20	50	150
Rape oil, refined	1220	380	...	18·48	5·76	...	660	224	...	12·22	4·15	...
Cod liver oil	760	262	...	11·51	3·97	...	430	165	...	7·96	3·06	...
American lubricating oil, pale, 0·905	905	215	...	13·71	3·26	...	475	140	...	8·80	2·59	...
Russian lubricating oil, pale, 0·908	4320	595	...	65·5	9·01	...	2340	355	...	43·33	6·57	...
American cylinder oil, pale	...	...	750	...	...	11·36	...	...	75	...	...	1·39
,, ,, ,, dark	...	...	1005	...	...	15·23	...	...	95	...	..	1·76
"Valvoline" cylinder oil	...	...	885	...	...	13·41	...	...	85	...	..	1·57

It will be gathered that the viscosity of lubricating oils diminishes rapidly with the increase of temperature; the decrease is, however, much greater in the case of mineral oils than in that of vegetable and animal oils. This is one of the reasons why blends of vegetable and animal oils with mineral oils give better results than mineral oils alone. Hence in many cases it will be found desirable to determine the viscosity of a lubricating oil at higher temperatures; if possible, at the temperature which the oil will reach in actual use.

A somewhat high viscosity of a given sample (as compared with the viscosity of a corresponding oil recorded in the tables, Chapter V. p. 208) may direct attention to an imperfectly purified oil, containing asphalt-like bodies (p. 944), or to oils thickened artificially with "oil thickener" (aluminium oleate), or with caoutchouc.[1]

The **freezing point** or **cold-test** of fatty oils is determined by the methods described in Chapter V. p. 183.

Holde[2] has drawn attention to the necessity of fixing by agreement the length of time and the manner in which a sample should be cooled before the cold test is carried out, since the actual cold test depends to a considerable extent on the preliminary treatment of the oil. This holds good of mineral oils as well as of fatty oils. Thus *Holde* has shown that the solidifying points of oils, which were stated by various observers as lying below 0° C., will solidify at 0° if allowed to stand at this temperature for several hours. It is well known that stirring assists solidification; hence different results will be obtained according as the oil has or has not been stirred during the cold-test.

Similar divergencies are noticeable in the examination of mineral oils containing paraffin wax, the separation of paraffin wax taking place at varying temperatures according to the manner of manipulation and cooling previous to the examination of the oil. A number of cold-test determinations have been given in Chapter V. p. 208.

The "cold-test" or setting point of mineral lubricating oils is not of so great an importance in this country as in the United States and on the Continent, where the danger exists of machinery being damaged by oil becoming solid in the lubricators. In these countries Railway Companies specify the temperature at which the lubricating oil must remain fluid.

The Scottish Mineral Oil Association directs that the setting point of mineral oil be determined in the following manner:[3]—Place the sample in a test-tube, having a diameter of one inch and a quarter, to the depth of about two inches. Immerse the test-tube in a freezing mixture and stir the oil slowly with a thermometer until it has cooled down considerably below the temperature at which solid paraffin wax first appears. Then remove the test-tube from the freezing mixture, stir constantly with the thermometer, and observe the temperature at which the last trace of solid paraffin wax dis-

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[1] Holde, *Die Untersuchung der Schmiermittel*, p. 122.
[2] *Mitth. a. d. Konigl. Tech. Versuchs. Anst.* 1895, 287.
[3] *Journ. Soc. Chem. Ind.* 1891, 347.

appears. Repeat the test until concordant results are obtained; the temperature so found is the setting point.

According to the directions of the New York Produce Exchange, the sample to be tested is poured into a beaker 4 in. deep by 3 in. in diameter, until nearly filled. The beaker is immersed in a freezing mixture of specified temperature, the temperature being controlled by a fixed thermometer; a second thermometer is then immersed in the oil, reaching half way down the beaker. The lubricating oil should still flow on inclining the beaker, when both thermometers register the same temperature. It should be noted that the oil is not stirred, and that therefore the conditions obtaining in practice are simulated to some extent, although the factor of time is neglected.

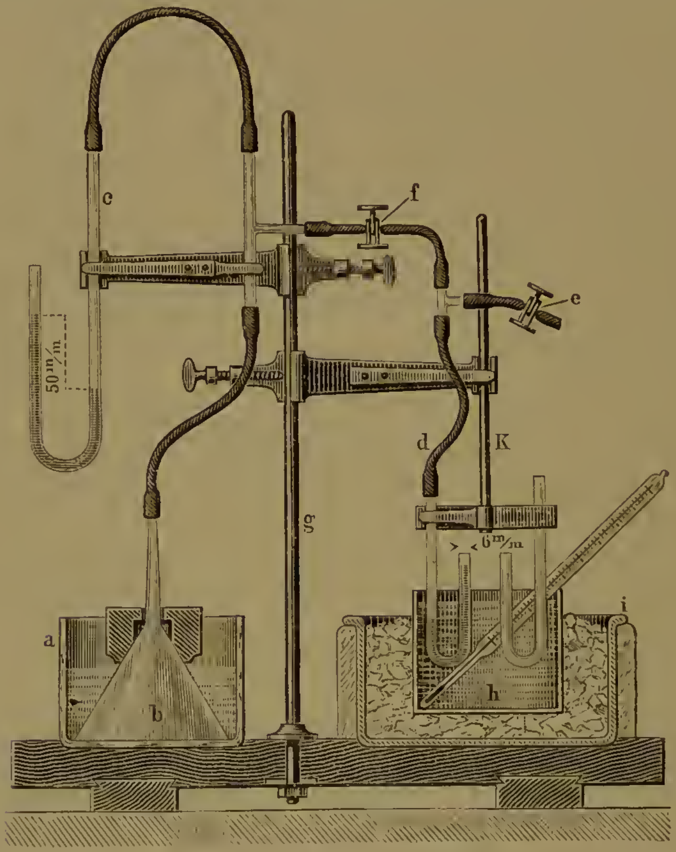

Fig. 64.

More complicated than the American test is the cold-test prescribed by the Prussian State Railway Direction. According to their rules "winter oil" must remain fluid at – 15° C., "summer oil" at – 5° C. This is considered to be the case if the oil cooled to – 15° C., or – 5° C., as the case may be, and subjected to the constant pressure of a water column of 50 mm., will rise in a glass tube of 6 mm. internal diameter at the minimum rate of 10 mm. per minute. The apparatus prescribed for this test is shown in Fig. 64.

The sample, freed from water and mechanical impurities, is introduced in a U-tube of 6 mm. internal diameter (two tubes are shown in the figure). This is immersed in a vessel *h*, filled with the freezing mixture of the specified temperature, and surrounded by vessel *i*, which is also filled with the freezing mixture. The temperature is controlled by a thermometer. The U-tube should stand at least one hour without being disturbed in the freezing mixture, the level of the oil being about 10 mm. below that of the freezing mixture. The tube is then carefully drawn out so far that the level can be observed, when the india-rubber *d* is slipped over its end whilst pinch-cock *e* is open. Close *e* and, by opening pinch-cock *f*, allow a pressure of 50 mm. (generated by pouring water into vessel *a*, in which the weighted funnel *b* is placed, and controlled exactly by manometer *c*) to act on the oil.

Chemical Tests

The general *chemical tests* have for their object (1) the identification of the oil; (2) the examination for purity of the oil (absence of adulterants); (3) determination of water; (4) determination of ash; (5) determination of free acid; (6) liability to gum or become oxidised; liability to spontaneous combustion; (7) loss by evaporation; (8) determination of paraffin wax; (9) determination of the flash point and of the ignition point.

Before a lubricating oil is tested it should be freed from any grit or solid tarry particles by filtering through filter paper or a sieve of very fine mesh.

(1) The methods employed for the **identification** of the fatty oils and liquid waxes have been given in previous chapters. If a mineral oil be given, the examination as to the origin of the oil is but rarely required. Expeditious methods for the discrimination between hydrocarbons derived from American, Russian, Galician, Roumanian, Borneo, etc., petroleum, have not yet been worked out, as the chemical composition of the hydrocarbons in the higher boiling portions is practically unknown as yet.[1] Shale oil hydrocarbons seem to be characterised by the comparatively high amounts of bromine they absorb, as compared with mineral oils derived from petroleum, owing to the presence of a considerable amount of olefinic hydrocarbons. In the absence of methods allowing a discrimination between shale oil and lignite oils,[2] physical indications (such as colour, fluorescence), smell, and also taste, afford safer guidance in the determination of the origin of these oils than have been obtained hitherto by purely chemical methods.

Blended oils, *i.e.* oils consisting of a mixture of fatty oils ("blown oils," see below), liquid waxes, and mineral oils are recognised by the general methods of analysis given in Chapters VI.-IX.

The determination and examination of the unsaponifiable matter

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[1] Cp. Aisinmann, *Chem. Revue*, 1897, 162.

[2] Cp. *Jahrbuch der Chemie*, 7, 384, 388.

is of great importance; it is carried out by the methods detailed in Chapter IX.

Small quantities of fatty oils in mineral oils are detected by ascertaining whether the sample has a saponification value. The quantity of the fatty oil can be readily ascertained by isolating the fatty acids, determining their mean molecular weight, and calculating the fatty acids to glycerides. If the amount of fatty oils be very small, the proportion of glycerol may be determined in a somewhat large quantity of the sample. If liquid waxes be present, the fatty acids must be calculated to esters.

The presence of "blown oils" is detected in the first instance by ascertaining the amount of "oxidised acids" (see chap. viii. p. 368) and by determining the acetyl value of the isolated fatty acids (cp. table given on p. 985, under "Blown Oils"). It should, however, be remembered that a high acetyl value may also be due to the presence of castor oil.

(2) The methods of detecting **rosin oils** in the unsaponifiable portion have been described on p. 384.

The *Liebermann-Storch* reaction may be supplemented by polarimetric examination. Rosin oils are dextro-rotatory; hence the presence of large quantities of rosin oils will be most readily detected by examining the unsaponifiable matter in the polarimeter. *Valenta* found in the case of a number of samples of rosin oils in Mitscherlich's polarimeter, for a length of 100 mm., rotations varying from 30° to 40° (dark specimens were previously clarified by means of charcoal). *Demski* and *Morawski* likewise found the rotation about 50°. Mineral oils are, as a rule, without action on the plane of polarised light, only two or three samples having been found to be dextro-rotatory, causing a deviation of 1°1′ to 1°6′.[1] As several vegetable oils are optically active, due care must be exercised, since the optically active substances contained in fatty oils pass into the unsaponifiable matter. It should further be borne in mind that hydrocarbons resulting from the destructive distillation of wool fat also exhibit optical activity (*Lewkowitsch*).

The quantitative determination of rosin oils in the "unsaponifiable portion" is a difficult problem, and cannot be solved satisfactorily in the present state of our knowledge. According to *Storch*[2] 10 to 15 grms. of the unsaponifiable matter (freed from fatty oils) are gently warmed in a flask with five times their weight of 96 per cent alcohol, and allowed to cool. The alcoholic solution, which will contain all the rosin oil present, is then transferred to a tared Erlenmeyer flask, about 7 cm. high; the undissolved mineral oil is again washed, without agitating, with a few c.c. of 96 per cent alcohol, which are added to the first solution. The Erlenmeyer flask is now placed in a beaker (to prevent too rapid condensation) and heated on a water-bath until the residue in the flask is free from bubbles. After cooling, the residue is weighed. The

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[1] Cp. Soltsien, *Chem. Centr. Blatt*, 1898, ii. 455.

[2] *Journ. Soc. Chem. Ind.* 1891. 276.

weight of this residue (A) represents that of the rosin oil *plus* that portion of mineral oil which has been dissolved by the alcohol. To remove the bulk of the dissolved mineral oil, the residue (A) is next treated with ten times its weight of alcohol, and the solution heated on the water-bath, as before, to remove the alcohol, when a second residue (B) is obtained, which still contains a small quantity of mineral oil. The necessary correction for this amount is found in the following manner:—Suppose 11·2 grms. of the sample have been treated with 50 grms. at first, and subsequently the residue (A) with 15·5 grms. of alcohol. Let the weight of (A) be 1·51 grms., and that of (B) 1·15 grms., then $50 - 15·5 = 34·5$ grms. of alcohol had dissolved $1·51 - 1·15 = 0·36$ grm.; hence 15·5 grms. had dissolved 0·162 grm. of mineral oil. There are therefore present in the sample $1·15 - 0·162 = 0·988$ grm., or 8·8 per cent of rosin oil. The true quantity lies between the weight of (B) and the corrected number.

Walker and *Robertshaw*[1] recently examined in my laboratory the various methods proposed for the quantitative determination of rosin oils. The process proposed by *McIlhiney*[2] for the estimation of rosin oils in fatty oils is based on the fact that the latter yield very low bromine substitution numbers, whereas rosin oils are characterised by high substitution numbers. *Walker* and *Robertshaw*, however, found that the reaction taking place when bromine is allowed to act on rosin oils depends so much on variations of time, temperature, and other not yet fully ascertained conditions, that it would appear a hopeless task to determine rosin oil quantitatively by this method in a mixture of rosin oil with mineral oil.

The method proposed by *Holde* for discriminating and determining rosin oil when admixed with mineral oils has also been shown to give uncertain results. Thus genuine rosin oils freed from rosin acids yielded considerable quantities of unsaponifiable portions which might be mistaken for mineral oil.[3] The best method for determining rosin oil in mineral oil is *Valenta's* process, as has been confirmed by the experiments of *Walker* and *Robertshaw*.[4]

Valenta's[5] process for detecting rosin oils in presence of mineral oils is based on the difference of their solubilities in glacial acetic acid at 50° C., a number of experiments on various mineral oils having shown that 100 grms. of glacial acetic acid dissolve 2·6 to 6·5 grms. of mineral oil, whilst under the same conditions 16·9 grms. of rosin oil are dissolved. The same relation is expressed by stating that 10 c.c. of glacial acetic acid dissolve 0·2833 to 0·6849 grm. of mineral oil and 1·7788 grms. of rosin oil. To perform *Valenta's* test 2 c.c. of the unsaponifiable matter are mixed in a test-tube with 10 c.c. of glacial acetic acid, and the tube, loosely closed by a cork, is immersed in a water-bath for five minutes, the contents being repeatedly shaken during that time. The mixture is then filtered

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[1] *Analyst*, 1902, 238.

[2] *Journ. Amer. Chem. Soc.* 1899, 1084; cp. also Chapter X. p. 389.

[3] Lewkowitsch, *Analyst*, 1903, 183.

[4] *Analyst*, 1902, 238.

[5] *Journ. Soc. Chem. Ind.* 1884, 643.

through a moistened filter, and the middle portion of the filtrate is collected. Part of this is weighed off accurately, and the amount of acetic acid determined by titration with normal caustic soda. The difference between the weight of the acid taken and the weight thus found is the amount of oil dissolved. *Allen*[1] points out that any rosin acids present in the rosin oil influence the solubility, and render the alkalimetric determination of the acetic acid inaccurate. *Allen* proposes, therefore, to neutralise the greater part of the acetic acid, dilute with water, and extract the rosin oil by agitation with ether.

Walker and *Robertshaw* found the percentage of rosin oil dissolved by acetic acid from two specimens of genuine rosin oils 16·8 and 16·6 per cent respectively, which agrees well with *Valenta's* figure of 16·9 per cent; the mineral oil which gave in *Valenta's* test 4·4 per cent (as against *Valenta's* numbers of 2·6 – 6·5 per cent) was mixed with an equal volume of a rosin oil of which 16·8 per cent was soluble. The mixture gave, on being tested, 10·84 per cent of dissolved oil, theory requiring 10·59 per cent.

A similar method based on the solubility of rosin oils in acetone—with which they are miscible in all proportions, whereas mineral oils require several volumes of acetone to be dissolved completely (*Demski* and *Morawski*,[2] *Wiederhold*[3])—has not yet been worked out quantitatively. Nor is it likely to lead to useful results, for Borneo mineral oil of specific gravity 0·97 to 0·99 simulates rosin oil not only in specific gravity, but also in that it is very readily soluble in an equal volume of acetone.[4] It is, however, easy to differentiate the Borneo oil from rosin oil by the *Liebermann-Storch* reaction.

Finkener's[5] proposal to differentiate rosin oil from mineral oil by a mixture of 1 volume of chloroform and 10 volumes of alcohol of specific gravity 0·8182 at 15·5° C. has not yet been worked out to a quantitative method. It may suffice, therefore, to mention that *Finkener* found that rosin oils are soluble in 10 volumes of this mixture (*Holde*[6] gives 12·5 volumes), whereas mineral oils are insoluble even in 100 volumes of the mixture.

(3) **Detection and Determination of Water.**—Oils containing water are turbid. In the case of mineral oils turbidity may be caused by separated paraffin wax; this will disappear on warming the sample. Water is readily detected by heating a sample of the oil in a test-tube, when frothing or bumping will indicate the presence of water. The determination of water is carried out in the case of fatty oils as described, p. 146. In the presence of mineral oils, especially those of comparatively low boiling points, the determination of water in the usual manner may easily lead to too low results, inasmuch as oils of low boiling points are volatilised with the water vapours. Hence, due care must be exercised. The proportion of water is best determined by dissolving a somewhat large quantity of the sample in petroleum ether, so that the water may settle out on standing.

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[1] *Com. Org. Anal.* ii. 465.

[2] *Journ. Soc. Chem. Ind.* 1886, 179.

[3] *Journ. f. prakt. Chem.* 1893 (47), 394.

[4] Jenkins, *Analyst*, 1902, 240.

[5] *Zeit. analyt. Chemie*, 1887, 652.

[6] *Chem. Revue*, 1898, 51.

(4) **Determination of Ash.**—The ash is determined by igniting an accurately weighed quantity of the sample under examination in a platinum dish and weighing the residue. In pure lubricating oils the ash will be *nil.* A definite residue may point to the presence of soda, potash, lime, or aluminium soap. In case a soda, potash, or lime soap was used, the residue will be found strongly alkaline to indicators. The presence of alumina in the ash would indicate that an "oil thickener," such as aluminium oleate, had been added.

Schweitzer and *Lungwitz*[1] recommend as a reagent for the detection of soaps in lubricating oils a saturated solution of metaphosphoric acid in absolute alcohol. In the presence of soaps a flocculent precipitate is observed.

(5) **Determination of Free Acids.**—The determination of free acids is of considerable importance in the examination of lubricating oils. The estimation of the free fatty acids is carried out in the manner described on page 277.

If the lubricating oil be a fatty oil, acidity may be due to free fatty acids or to incomplete removal of mineral acids, which latter have been left in the oil in consequence of incomplete washing after refining. Mineral acids are detected by shaking the sample with water to which a drop of methylorange solution has been added. Mineral oils are tested in the same manner for traces of inorganic acids. Naphthenic acids, so-called petroleum acids, are not removed by washing with water. Their proportion is determined by shaking 100 grms. of oil with 50 c.c. of decinormal alkali containing about 50 per cent alcohol, and titrating back the excess (*Zaloziecki*[2]). In case sulphonated oils, produced by the action of concentrated sulphuric acid, used in the refining process of oils, be suspected, 50 grms. of the oil should be boiled under a reflux condenser with strong hydrochloric acid. The aqueous layer is then tested for sulphuric acid.

As regards the permissible amount of fatty acids in lubricating oils, opinions differ. As a rule, railway companies specify in their contracts the *maximum* amount of free acid. The larger the proportion of free acids in an oil, the greater is the liability to corrode the metal surfaces of the lubricated journals. From the experiments made by *I. I. Redwood*,[3] *Aisinmann*,[4] and *Donath*,[5] it is not permissible to draw the conclusion that lubricating oils would behave in practice in the same manner as in laboratory experiments. Hence these experiments need not be detailed here.

It should be borne in mind that fatty oils undergo hydrolysis in high-pressure steam cylinders, and that the fatty acids thus set free will corrode the iron cylinder, forming metallic soaps. This is one of the reasons why fatty oils are no longer used alone for high-pressure steam cylinders. Metallic soaps formed by the action of the liberated fatty acids on the metal are somewhat soluble in mineral

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[1] *Journ. Soc. Chem. Ind.* 1894, 1178.
[2] *Chem. Revue*, 1897, 37.
[3] *Journ. Soc. Chem. Ind.* 1886, 362.
[4] *Dingl. Polyt. Journ.* 294, 65.
[5] *Ibid.* 294, 186.

oils (cp. Metallic Soaps, p. 1083), and are therefore less likely to cause obstructions than where fatty oils alone are used.

The opinion held generally that mineral oils do not attack metals is based more on chemical *a priori* deductions than on practical experience. Mineral oils also suffer oxidation to some extent, the magnitude of which depends largely on the care used in refining. This does not only hold good of shale oils, but in general of American, Russian, and other mineral oils.[1]

(6) **Liability to "gum."**—A good lubricating oil should neither dry on exposure nor "gum" (causing more fuel to be consumed in consequence of the drag upon the machinery), nor have a tendency to become acid. Satisfactory methods for ascertaining the liability of a lubricating oil to gum have not yet been worked out. Since oils belonging to the class of drying oils, as also fish oils, rosin oils, and to a smaller extent also the semi-drying oils of the cotton seed oil group, readily absorb oxygen, and thereby "thicken" or "gum," the unsuitability of these oils for lubricating purposes is evident. The detection of the presence of such oils in a sample has been described in Chapter XIV. The examination by the methods described in Chapter VII. under "Oxygen Absorption Test" may in some cases prove of assistance.

Gill[2] proposes to determine the gumming properties of lubricating oils with nitro-sulphuric acid, prepared by saturating sulphuric acid of 76° Bé, containing a few drops of nitric acid, with nitric oxide at 0° C. The amount of tarry matter formed thereby is stated to stand in a definite relation to the oxygen absorption as ascertained by *Fox's* method. This method, of which details were given in former editions of this work,[3] consists in determining the oxygen absorbed on heating an oil in a sealed tube with oxygen gas.

Badly refined oils have a tendency to resinify easily. Impurities due to incomplete purification may be identified by one of the following methods. It should, however, be noted that in some cases these impurities are purposely left in the oils, since complete removal of the asphalt-like and mucilaginous substances, naturally occurring in the crude oils, tends to reduce the viscosity and consequently the apparent lubricating value. *Martens* advises to shake equal measures of the sample and of sulphuric acid, specific gravity 1·53; in the case of a pure oil the acid should separate as a colourless or, at most, slightly yellow layer; there should be no separation of black flocks in the oil, nor should it be coloured brown. If the acid remains colourless, or is but slightly coloured, the experiment should be repeated at 100° C.; pure oils should not turn brown even under these conditions. (In the presence of fatty oils the sulphuric acid treatment would lead to altogether unreliable results). Attempts have been made to convert this test, in the examina-

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[1] Cp. Ostrejko, *Journ. Soc. Chem. Ind.* 1896, 26, 345, 645; Holde, *Die Untersuchung der Schmiermittel*, 1897, 88; Steuart, *Journ. Soc. Chem. Ind.* 1899, 239.

[2] *Journ. Amer. Chem. Soc.* 1902, 690.

[3] Cp. *Chemical Analysis of Oils, Fats, and Waxes*, 2nd ed. p. 714.

tion of mineral oils, into a quantitative one by operating as follows:—

20 c.c. of the sample are shaken in a graduated stoppered cylinder with 10 c.c. of concentrated sulphuric acid and 20 c.c. of petroleum ether; the increase in volume of the acid is read off after separation into two layers has taken place. Oils of good quality should yield to the acid no more than 1·2 to 2·4 c.c., *i.e.* 6 to 12 per cent. But it must be understood that these results lead to rough approximations only, as the "naphthenes," the characteristic hydrocarbons of the Russian petroleum, are soluble in concentrated sulphuric acid. *Holde*[1] showed that by treating lubricating oils with a mixture of alcohol and ether (3 : 4) resinous or "asphaltic" bodies containing oxygen are precipitated. Hitherto no reliable quantitative method has been worked out.[2] Another impurity which is also precipitated by the alcohol-ether mixture is caoutchouc, which is added to lubricating oils in order to raise their viscosity (*Holde*[3]).

Since fatty oils, which exhibit a pronounced tendency to gum, are also those which are liable to spontaneous combustion, the behaviour of a fatty lubricating oil in this respect may be determined by means of the "Cloth Oil Tester" (see Wool Oils, p. 957).

(7) **Loss by Evaporation.**—"Volatility Test."—In the case of fatty oils the point at which evaporation commences almost coincides with the temperature at which decomposition takes place, whereas in the case of mineral oils, consisting as they do of oils of different boiling points, evaporation—and consequently loss to the user of the oil—may set in below the temperature at which the bulk of the mineral oil volatilises.

The method ordinarily adopted to determine the loss by evaporation is to heat an accurately weighed quantity on a watch glass for several hours and to weigh the residue. Oils intended for the lubrication of machinery at normal temperatures would be kept for a few hours at 100° C. Cylinder oils are heated in a drying oven or in a suitable oil-bath (*Holde*[4]) at temperatures varying from 150° to 300° C.

Archbutt[5] recommends as a safer method to heat the oil in a current of air or superheated steam. 0·5 grm. of the sample is placed in a platinum tray, which is brought into a glass tube, and thus introduced into a copper tube, $\frac{7}{8}$ in. internal diameter and 2 ft. long. Round the copper tube is coiled a tube, $\frac{3}{8}$ in. diameter and about 10 ft. long, one end of which enters the wider copper tube and serves to heat the current of air or steam which is passed over the oil. The coiled tube is fixed in an air-bath and heated by a row of small gas jets to the desired temperature, which is controlled by a thermometer. A measured quantity of air is passed over the oil at the rate of 2 litres per minute for exactly one hour; the oil is then

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[1] *Mitth. Königl. Techn. Vers. Anst.* 1895, 174; 1902, 253; 1903, 57.

[2] Holde, *Die Untersuchung der Schmiermittel*, p. 183. Cp. also Aisinmann, *ibid.* 1895, 282; Singer, *Chem. Revue*, 1897, 93.

[3] *Die Untersuchung der Schmiermittel*, p. 122.

[4] *Mitth. Techn. Vers. Anst.*, Berlin, 1902, 67.

[5] *Journ. Soc. Chem. Ind.* 1896, 326.

withdrawn and weighed. Good locomotive cylinder oils should not lose more than 0·5 per cent at a temperature of 370° F. (188° C.).

(8) The determination of **paraffin wax** (German, *Paraffin*) will but rarely be required. Lubricating oils containing too much paraffin wax would not prove satisfactory in the "cold test," and would therefore be rejected at the outset.

Holde examined the processes proposed by *Pawlewski* and *Filemonewicz*, *Zaloziecki*, and *Höland* for the estimation of small quantities of paraffin wax,[1] and rejected them as not admitting of general application. *Holde*[2] recommends the following method, which is a modification of the one originally suggested by *Engler* and *Boehm* :—

10 to 20 c.c. of oils poor in paraffin wax (such as Russian distilled oils, solidifying below − 5° C.), or 5 grms. of oils rich in paraffin wax (such as American, Scotch, Galician, solidifying at or above 0° C.) are placed at the ordinary temperature in an Erlenmeyer flask of 150 to 200 c.c. capacity, and so much of a mixture consisting of equal parts of nearly absolute alcohol (98·5 per cent) and ether are added that a clear solution is obtained. The flask is then immersed in a freezing mixture of from − 20° to − 21° C. Whilst the solution is being vigorously agitated, so much of the alcohol-ether mixture is added that the drops of oil just disappear and only crystals or flocks of paraffin wax are noticeable. The crystals are filtered off at the same low temperature on a cooled filter and washed with the alcohol-ether mixture, previously cooled down to − 20° to − 21° C., until 5 to 10 c.c. of the filtrate no longer give an oily residue. Prolonged washing beyond this point leads to loss. The paraffin wax retained on the filter is rinsed into a capsule with benzene. The solvent is then evaporated off and the residue dried at 105° C. for 15 minutes. Prolonged heating in the air-bath is avoided, as otherwise loss may occur.

The objections raised by *Eisenlohr*[3] against this method as leading to incorrect results in the case of soft paraffin waxes have been met by a modification of the original process (*Holde* and *Allen*).[4]

(9) The **flash point** is usually determined by the "open test." About 50 c.c. of the oil under examination are placed in a porcelain crucible or a small wide-necked flask, so as to fill about three-quarters of the vessel. The vessel is embedded in a sand-bath a little above the level of the liquid, and a thermometer inserted in the oil. The sand-bath is then so heated that the temperature rises slowly; from time to time a small flame is brought on to the surface of the oil. That temperature at which a slight explosion or "flash" takes place is noted as the flash point. It is advisable to ascertain by a preliminary

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[1] Cp. Eisenlohr, *Zeits. f. angew. Chem.* 1897, 300.

[2] *Chem. Revue*, 1897, 4, 21.

[3] *Zeit. f. angew. Chem.* 1897, 332.

[4] *Chem. Rev.* 1898, 112, 131 ; cp. also Clifford Richardson, *Journ. Soc. Chem. Ind.* 1902, 690.

test the temperature at which the "flash" will take place, and then ascertain the flash point more accurately. The results obtainable by this method—which is sufficiently accurate for practical purposes, since it is only necessary to ascertain whether an oil is dangerous or not—will be found to vary between 2-5° C.

It is necessary that the oils previous to being tested should be freed from water.

The lowest value for the flash point by the "open test" should be about 175° C. (350° F.) for lubricating oils, and about 260° C. (500° F.) for cylinder oils. The following table gives *Künkler's*[1] observations on a few lubricating oils :—

Oils.	Spec. Grav. at 17·5° C.	Flash Point °C.	Viscosity (Engler)	
			At 50° C.	At 100° C.
Russian cylinder oils	0·911-0·923	183-238	10·2-16·2	2·0-2·8
,, machine oils	0·893-0·920	138-197	5·8-6·3	1·5-1·8
,, spindle oils	0·893-0·895	163-167	3·1-3·4	1·4-1·5
American cylinder oils	0·886-0·899	280-283	...	4·1-4·8
,, machine ,,	0·884-0·920	187-260	4·2	1·6
,, spindle ,,	0·908-0·911	187-200	3·1-3·3	1·4-1·6
Rape oil, crude	0·920	265	4·0	1·7
,, ,, refined	0·911	305	4·9	2·0
Olive oil	0·914	305	3·7	1·8
Castor oil	0·963	275	16·4	3·0
Linseed oil	0·930	285	3·2	1·7
Tallow	0·951	265	5·2	2·5

In Germany some railway companies direct that the *Treumann* cup be used for this test.[2]

When greater accuracy is required than is furnished by the "open test," or in case of a dispute, the adoption of "close test" apparatus is advisable. The *Scottish Mineral Oil Association*[3] prescribes the employment of the *Pensky-Martens* apparatus, which is also the apparatus used officially in Germany.

The Pensky-Martens apparatus (Figs. 65 and 66) is modelled on the Abel Petroleum Tester.

E (Fig. 65) is the oil vessel, which is placed in a metal heating-vessel H, protected from the radiation of heat by the mantle L. The oil cup E is closed by a tightly-fitting lid (shown in plan 2). Through the centre of the lid passes a shaft carrying the stirring arrangement, which is worked by means of the handle J. In another opening of the cover is fixed a thermometer. The lid is perforated with several orifices, which are covered or open, as the case may be, by a sliding cover. This can be rotated by turning the vertical spindle by means of the milled head G. By turning G an opening of the

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[1] *Journ. Soc. Chem. Ind.* 1890, 197.

[2] Cp. Treumann, *Zeit. f. öffent. Chemie*, 1898, 855.

[3] *Journ. Soc. Chem. Ind.* 1891, 347.

slide can be made to coincide with an orifice in the cover, and simultaneously a very small flame, burning at the movable jet E (Fig. 66), is tilted on to the surface of the oil. This contrivance is shown on a larger scale in plan 2, Fig. 65.

The test is performed by filling the oil into the oil-cup up to a certain mark, fixing the cover, and heating the oil somewhat rapidly at first, until its temperature is about 30° C. below the expected flash point. The temperature is then allowed to rise very slowly only, by making suitable use of the wire gauze shown in the figures, so that the rise of temperature does not exceed about 2° C. within half a minute. From time to time the milled head G is turned and the flame tilted into the oil cup. The temperature at which a slight explosion is produced is the flash point of the oil.

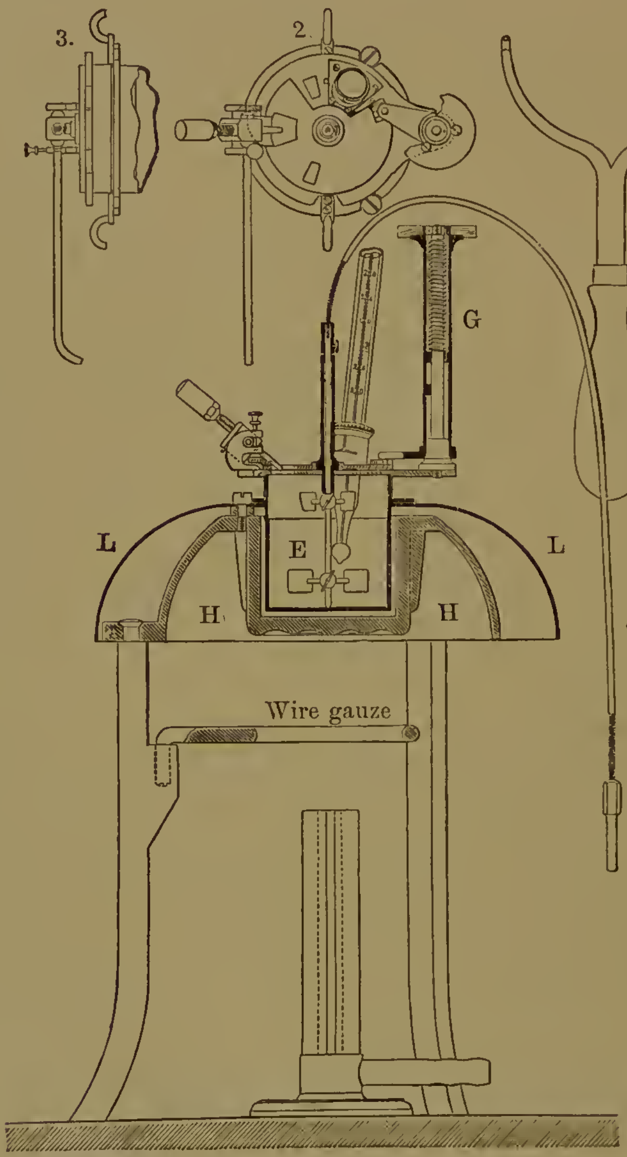

Fig. 65.

In this country *Gray's* apparatus (Fig. 67) is used frequently. It consists of a brass oil cup, A, of 2 in. diameter by 2·2 in. in depth (the same dimensions as in the Abel Petroleum Tester). The height to which the cup is filled is indicated by a line cut round the inside; it runs 1½ in. from the bottom. The cup is closed by a tightly-fitting lid, through the centre of which a steel shaft passes to the bottom, carrying two sets of stirrers, one above and the other below the surface of the oil. On the top of the steel shaft there is fixed a small bevelled wheel, H, with milled edge, and geared with a vertical bevelled wheel, G, actuated by a small handle, B. Thus the stirrers are set in motion. The lid is provided with four openings, one of which serves for the insertion of a thermometer, whereas the other three provide means for producing the "flash." These three orifices are, as a rule, closed by a loose flat cover, S, provided with openings which coincide with the ports in the fixed lid when the cover is turned one quarter round. One of the latter is immediately in front of the test-lamp, D, which can be tilted whenever required, whereas the other two ports, one on each side, admit air to produce the explosive mixture.

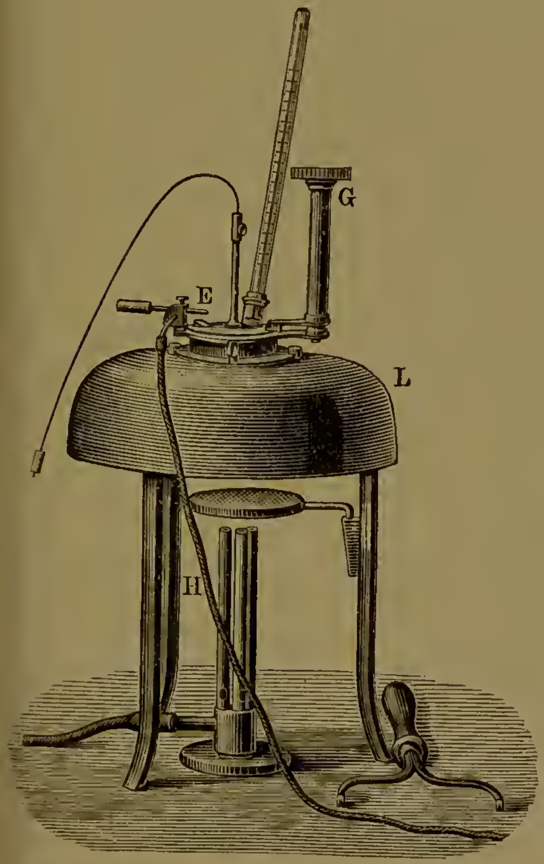

Fig. 66.

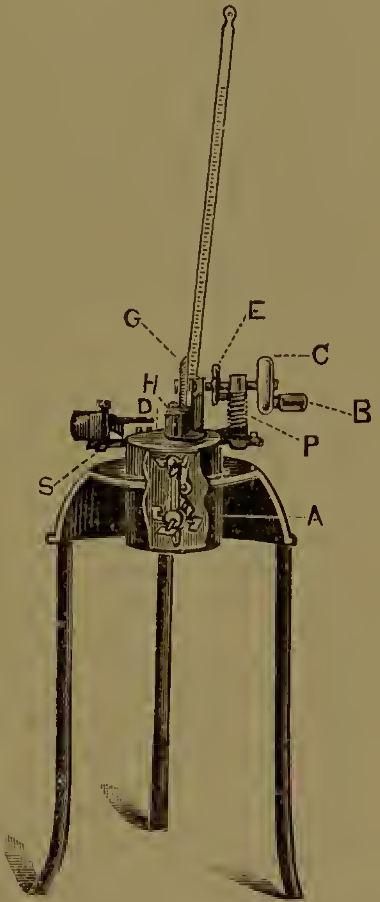

Fig. 67.

To perform the test, fill the cup to the mark with the sample, light the test-lamp and adjust the flame, so that it is about ⅛ in. high. Then heat the oil cup by means of a Bunsen burner or a sand-bath, whilst rotating the stirrers, so that the temperature of the oil rises about 5° C. per minute at first, then less rapidly when the point is reached at which the oil is expected to flash. Whilst the bevelled wheels are in gear the sliding cover is held in its normal position by the spring P. Then draw the horizontal shaft, which has a little lateral play in its bearings, slightly to the right, whereby the stirrers are thrown out of gear. Turn the handle a quarter of a round, when the loose cover is rotated, the ports opened, and at the same time the test-lamp tilted into the opening. Reverse the handle immediately, whereby the ports are closed automatically. The temperature at which a slight explosion is produced is noted as the flash point of the oil. If no flash was produced, continue the heating, throw the stirrers into gear, and proceed as before.

The **ignition point** may be defined as that temperature at which the oil will continue to burn when a flame has been brought into contact with the surface of the oil for a few seconds. The determination of the ignition point, if required, is carried out in a similar manner to that described above under "flash point."

A crucible of about 40 mm. diameter and 40 mm. high is filled within 5 mm. of its brim, and embedded to half its height in a sand-bath. The crucible is heated at first rapidly until the flash point has been reached, then the gas-burner is turned low and the temperature allowed to gradually rise 10°-15° C. above the flash point; after every rise of 2° C. a small flame is approached to the surface until the oil burns quietly. The crucible must be protected from draught by a convenient arrangement.

It should be noted that the flash point and ignition point give no indications whatever as regards the lubricating value of an oil. Their significance lies in that they indicate whether a lubricating oil is suitable under given conditions. Since it so happens that oils having high flash points and ignition points are also the most viscous ones, unwarranted conclusions have been drawn from high flash and ignition points of lubricating oils.

If it be required to ascertain whether mineral oils have been debloomed artificially, **nitrobenzene** or **nitronaphthalene** must be tested for.

Nitrobenzene is readily detected by its smell, especially on warming.

For the detection of **nitronaphthalene** in mineral oils, *Leonard*[1] gives the following method based on the reduction of nitronaphthalene to naphthylamine:—A small quantity of the oil is gently warmed with zinc-dust and dilute hydrochloric acid, and the mixture agitated from time to time. The fæcal odour characteristic of α-naphthylamine will then be noticed. The acid aqueous liquid is then drawn off and tested in the following manner:—A portion of the liquid is neutralised with ammonia; on adding ferric chloride a

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[1] *Journ. Soc. Chem. Ind.* 1894, 69; cp. also Holde, *ibid.* 1894, 906.

blue precipitate is obtained which rapidly becomes purple. The remainder of the liquid may be made alkaline with soda and extracted with ether. The latter is then evaporated, and the residue dissolved in a little alcohol. On the addition of a drop of a solution of sodium nitrite, which has been acidified with acetic acid, a yellow colour is produced. On adding hydrochloric acid the colour is changed to crimson.

Mechanical Tests.

The physical and chemical examination described above by no means exhaust the tests to which a lubricating oil must be submitted in order to arrive at a definite opinion as regards its suitability for a given purpose. It may therefore be useful to point out once more that the determination of the viscosity does not furnish a complete answer as to the lubricating value of a given oil, for a substance may be viscous and yet not be a good lubricant, as not having the "body" or "oiliness" (German—*Schlüpfrigkeit*) which shows itself by the "smoothness" felt when the oil is rubbed between the fingers. On the "smoothness" or "oiliness" depends the thickness of the oil-film which a lubricant forms when applied to running machinery. "Smoothness" or "oiliness" depends on the nature of the oil, and is greatly affected by the pressure, speed of the running machinery, and also by the temperature to which the lubricant is exposed.

It is impossible to ascertain the behaviour of a given oil in these respects by means of the physical and chemical examinations described above. Hence they must be supplemented by mechanical tests.

Railway Companies and other large consumers of lubricants test the lubricating power by means of specially designed apparatus, simulating as nearly as possible the conditions obtaining in practice.

A considerable number of mechanical oil-testing machines have been described and patented. But since this subject must necessarily fall outside the scope of this work, the reader is referred to the sources given in the footnote.[1] It should, however, be noted that opinions arrived at on the strength of tests carried out by means of oil-testing machines are not always confirmed by practice, since a great deal depends on the manner in which a lubricating oil is applied.

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[1] Tower, *Proc. Inst. Mech. Eng.* 1883-1891 ; Redwood, *Journ. Soc. Chem. Ind.* 1886, 121 ; Carpenter-Leask, *Soaps and Candles*, pp. 258-313 ; Thorpe's *Dictionary of Applied Chemistry*, vol. ii. p. 474 ; Thurston, *Treatise on Friction and Lubrication*, pp. 248-263 ; B. Redwood, *Petroleum*, p. 634 ; Goodman, *Recent Researches in Friction ; Proc. Inst. Civil Engineers*, vol. 85 ; Archbutt and Deeley, *Lubrication and Lubricants*, p. 319 ; Holde, *Die Untersuchung der Schmiermittel*, p. 224 ; Weiss, *Dingl. Polyt. Journ.* 309 (1898), 76 ; H. V. Blake, English Patent, 25492, 1902 ; K. Wilkens, English Patent, 20998, 1902 ; English Patent, 15897, 1902 (Dettmar's Oil-Testing Apparatus).

SOLID LUBRICANTS—GREASES

Under this head fall all those lubricants which are solid or semi-solid (jelly-like, gelatinous) at the ordinary temperature. The greases are conveniently subdivided into

(α) Solidified Oils;
(β) Rosin Greases; Axle Greases;
(γ) Lubricating Greases; Lubricating Pastes.

(α) Solidified Oils

The solidified oils contain as a rule no water; they consist preponderantly of mineral lubricating oils (of high specific gravity), which have been solidified or gelatinised by means of soda, lime, or aluminium soap. The manufacture of "solidified oils" of this kind is exemplified by *Eckenberg's* patent:[1]—Wool fat fatty acids or crude wool fat are dissolved in paraffin oil, and about half the amount of alkali required for the neutralisation of the free fatty acids is added. The mass is then heated so as to drive off the water and poured, whilst hot, into moulds.

Lime soaps—of fatty acids or rosin acids—also frequently enter into the composition of solidified oils.

Lubricants of this kind possess sufficient consistence to be cut into lumps. The "vaseline bricks" belong to this class of solidified oils.

The analysis of these products embraces the determination of the ash, of the amount of unsaponifiable matter, and of the combined fatty and rosin acids. Each of the constituents named is then further examined.

(β) Rosin Greases—Axle Greases

The rosin greases are essentially a solution of calcium resinate in rosin oil. The manufacture of these greases consists in stirring dry, slaked lime, freed from all gritty particles by careful sieving, into mineral oil, taking care that a homogeneous mixture is obtained.

The proportions usually taken are:—5 parts of lime to 100 parts of mineral oil. Into this mixture ("stock") a distilled rosin oil ("set"; German—*Harzstockoel*), containing rosin acids (see p. 383), is run in, and the mass is carefully stirred for a short time and then allowed to stand. The rosin acids combine with the lime, and the lime soap so formed is capable of holding both the mineral oil and the rosin oil in a semi-solid emulsion.

(γ) Lubricating Greases—Lubricating Pastes

(French—*Graisses consistantes*, *Graisses lubrifiantes*. German—*Consistente Fette*, *Starrschmieren*, *Zähschmieren*) represent essentially mix-

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[1] English Patent, No. 16,541, 1896.

tures of solid fats, fatty oils, mineral oils, rosin oils, and lime, soda, aluminium, or zinc soaps. These lubricants also contain a certain amount of water, up to 35 per cent.

The manufacture of these lubricants consists in dissolving the fats in mineral oil and boiling with a solution of caustic soda or milk of lime, etc., using the base in a quantity which is insufficient to completely saponify the neutral fats.

If it be desired to have only a small quantity of water in the finished product, as is necessary in a grease containing much lime soap, a mixture of dry lime and mineral oil may be prepared (as described above, p. 952), and after adding a small quantity of water, the partial saponification of the then added fat is completed by heating. By introducing rosin oil containing rosin acids solidification may be effected at somewhat lower temperatures.

Another mode of manufacturing these lubricants consists in simply dissolving a soda soap containing a normal amount of water in paraffin oils. If a lead soap be used the so-called *Galena oils* are obtained.

To these greases are also added inert substances, such as talcum or plumbago, with a view to increasing their lubricating power. Therefore the talcum and plumbago must not be looked upon as adulterants.

Frequently greases of this kind are perfumed with mirbane oil and coloured yellow with aniline dyes.

Special kinds of this class of greases are those known as *Stauffer's lubricants*, *Tovote greases*, etc.

Railway waggon greases also belong to this class, and are generally prepared by melting together tallow and palm oil at a temperature of about 100° C., running in a solution of sodium carbonate, previously heated to the same temperature, and stirring the mass until it solidifies. Since the palm oil contains free fatty acids, a palm oil soap is formed, which holds the unsaponified part of the palm oil and unsaponified tallow in an emulsion.

The compositions of most of these lubricating greases are considered by their manufacturers as valuable secrets. Each lubricating grease requires, therefore, a special method of analysis. The examination comprises the determination of the following constituents:—1. Water; 2. Fatty acids combined as soap (free fatty acids, if any); 3. Unsaponifiable matter; 4. Unsaponified fat; 5. Ash. Each of the constituents named under Nos. 2, 3, and 4 must be further examined according to the methods detailed in Chapters V.-X.

The lubricant is first dried at 100° C. and the amount of water is thus found. Simultaneously the anhydrous lubricant is obtained in a state ready for subsequent examination. The residue is next extracted with a suitable volatile solvent, when added mineral matters—weighting substances—and practically the total amount of soaps remain undissolved, whereas the unsaponifiable matter and the unsaponified fat (and free fatty acids if any) pass into solution.

The undissolved portion is examined for soluble (soda) soap by boiling out with water; if insoluble soaps be present, recourse must be had to the method described under "Metallic Soaps" (p. 1083). From the dissolved portion the solvent is evaporated off, and the residue so obtained is boiled with alcoholic potash. The unsaponifiable matter is then determined, and examined by the methods detailed in Chapter IX. The fatty acids and rosin acids liberated from the soap solution may then be further examined. The chemical analysis gives, however, no clue as to the lubricating value.

Hot neck greases (see p. 1037).

V. WOOL OILS—CLOTH OILS[1]

French—*Huiles d'ensimage.* German—*Wollspickoele, Wollschmälzoele, Wolloele.*

Under the trade term "wool oils" or "cloth oils" are comprised all those oils that are used by woollen manufacturers for lubricating the wool before spinning, or for oiling the rags before grinding and pulling.

The best wool oils consist of pure fatty oils, such as olive oil, lard oil, neat's foot oil. Besides these, oleic acid ("saponification oleine" or "saponified oleine," "distillation oleine" or "distilled oleine," see p. 1057) is used largely as a cheaper kind of wool oil. It commends itself also for the reason that it is easily removable in the scouring process; yet it should not be used for the finest goods, as the action of the fatty acid on the metal of the scribblers is apt to cause defects in the woven goods. The tendency to produce cheap wool oils, especially those which are used for the lowest textile goods, has led to the employment of "distilled grease oleine" (see chap. xi.), and even "waste oils," such as "black recovered oil," "seek oil," and "brown grease oil" (cp. Waste Fats, chap. xvi.). The last named oils contain considerable amounts of unsaponifiable matter. Besides these oils there are found in commerce large quantities of "manufactured oils," representing blends of the above named wool oils, as also blends containing mineral oils. The principles upon which the valuation of wool oils should be based are the following:—

(1) Wool oils should be *easily removable in the scouring process.* They should therefore be free from drying and semi-drying oils or their fatty acids, as also from rosin acids and rosin oils, since all these substances offer great resistance to removal in the scouring process, become sticky, leave an unpleasant odour on the fabric, and cause stains in the finished cloth. For finer goods even small quantities of hydrocarbons in the oils are objectionable.

Although the mineral oils readily form emulsions with soap solutions, practical experience shows that they are not so easily

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[1] Cp. Lewkowitsch, *Journ. Soc. Dyers and Colourists*, 1896, 60; *Journ. Soc. Chem. Ind.* 1896, 459.

removable as their behaviour with soap solutions might lead one to anticipate. Therefore, for best goods wholly saponifiable wool oils only should be used. The low class wool oils containing large proportions of hydrocarbons can only be removed by the employment of strongly alkaline soaps.[1]

(2) Wool oils should *develop as little heat as possible* both in the stored raw material and during the working of the oiled material. *Drying and even semi-drying oils* easily give rise to a development of heat sufficient to cause spontaneous combustion or to produce heat in the scribbling and carding process.

(3) The liability of oils *to favour the spreading of fire* should be as small as possible. Since the Fire Insurance Offices put great strictures on the users of wool oils, and assess the insurance premiums according to the quality of the oils, it may be found useful to quote the order in which the oils are arranged in the schedules of the Fire Insurance Companies in this country :—

Free from any extra charge are—Olive (Gallipoli) oil, lard oil, oleine ("saponified" or "distilled") not containing more than 10 per cent of unsaponifiable matter, fish oil, or a manufactured oil ("purified by distillation or saponification," whatever this may mean) containing not more than 30 per cent of unsaponifiable matter,[2] and having a flash point of not under 340° F. (167·8° C.).

A higher rate is charged for—Manufactured oils containing more than 30 per cent, but not more than 50 per cent, of unsaponifiable matter.

A still higher rate is charged for—Black (recovered) oil (chap. xvi.), containing not more than 50 per cent of unsaponifiable matter.

The highest rate is charged for—Manufactured oils containing more than 50 per cent of unsaponifiable matter, or mineral oil, oil of pine, linseed oil, rape oil, cotton seed oil, or any other seed oil.

Neat's foot oil and tallow oil are not mentioned in these schedules, although they are very useful wool oils and quite harmless, whereas, curiously enough, fish oil, which is a very dangerous oil (since cotton rags oiled with fish oil will ignite spontaneously) is permitted free of extra charge; whilst cotton seed oil, which is equally dangerous, is rightly placed amongst the oils charged at the highest rate.

Mineral oils in themselves are not liable to spontaneous combustion; experience shows, however, that once a fire has broken out, they cause the rapid spreading of it; it is for this reason that strictures are laid on extensive use of mineral oils.

Therefore *the determination of the unsaponifiable matter and of the flash point* are of the greatest importance in the analysis of wool oils.

The examination of wool oils comprises the test for purity, including the determination of the unsaponifiable matter. Some

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[1] Cp. Lewkowitsch, *Journ. Soc. Dyers and Colourists*, 1894, March; *Journ. Soc. Chem. Ind.* 1894, 258; *Journ. Soc. Dyers and Colourists*, 1896, 60; *Journ. Soc. Chem. Ind.* 1896, 459; Spennrath and Walther, *Journ. Soc. Chem. Ind.* 1895, 362; Ulrich, *Augsburger Seifensieder Zeitung*, 1903, 688.

[2] The Austrian Fire Insurance Companies allow only 15 per cent of unsaponifiable matter.

analysts ascertain the saponifiable only, *i.e.* the sum of the neutral fat and fatty acids, by boiling the sample with alcoholic potash (p. 227), and calculating the amount of potassium hydrate (KOH) used to oleic acid, thus obtaining the "unsaponifiable matter" by difference.[1] This method must be rejected as leading to erroneous results in many cases; hence the unsaponifiable matter should be determined direct by extraction with a solvent (chap. ix.).

Another error committed by some analysts is to return the "unsaponifiable matter" as mineral oil, a misnomer which may lead to great inconvenience to the user of the oil. The unsaponifiable matter should only then be returned as mineral oil, when the detailed examination warrants such a statement. Even if the unsaponifiable matter be liquid or fluorescent, it must not be judged to consist of mineral oils, as the hydrocarbons formed by destructive distillation of wool fat[1] have the same appearance. In case wool fat hydrocarbons be present, they will show the isocholesterol reaction (p. 141). It should be noted that since the fire insurance companies fix their rates according to the amount of unsaponifiable matter, *rosin* is now added fraudulently. This is detected and determined in the saponifiable part (*i.e.* soap solution) as described in Chapter X. p. 394.

The determination of the flash point is carried out as described already (p. 946). The flash point of a wool oil should not be below 170° C. (340° F.)

A rapid method of determining the liability of wool oils to spontaneous combustion is afforded by using *Mackey's* "Cloth Oil Tester."

This apparatus (Fig. 68) consists essentially of a cylindrical metal water-bath, provided with a lid having a nozzle for inserting a thermometer, and fitted with two tubes A and B for air currents which pass through the cylinder in the directions of the arrows. Inside the apparatus is placed a cylinder C of wire gauze, containing a ball of cotton wool oiled with the sample under examination. To perform the test weigh out 14 grms. of the sample into a shallow dish containing 7 grms. of pure cotton wool. Tease out carefully the cotton wool by hand, so that the oil is thoroughly distributed throughout the mass. This teasing and incorporation of the oil with the cotton must be done with the greatest care, as the success of the experiment depends on the even distribution of the oil. Transfer the oiled cotton wool to the cylindrical cage C, holding the thermometer in its place, whilst the cotton wool is being packed around it. Bring the water in the jacket to vigorous boiling, place the cage in the air-bath, slip the lid down over the stem of the thermometer, and fix it in its place[2] by means of the clamp D. Keep the water in the bath

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[1] Cp. Lewkowitsch, *Journ. Soc. Chem. Ind.* 1892, 142. The importance of this question with regard to insurance risk has been clearly stated in a paper by *Mackey*, read before the Insurance Institute of Yorkshire. Cp. *The Textile Manufacturer*, 1894, 18.

[2] The thermometer provided with the apparatus bears a red mark on the stem; it should be so fixed that the red mark is just visible. The apparatus is supplied by Reynolds and Branson, Leeds.

boiling, and note the temperature after the lapse of one hour. Care must be taken that no moisture enter the air-bath.

If the thermometer registers over 100° C. at the end of the first hour, the oil under examination must be considered as dangerous. In the case of very dangerous oils the temperature will run up to 200° C. within one hour and a half. Should the temperature rise very rapidly above 150° C. it is best to withdraw the thermometer, as the oiled cotton wool may ignite.

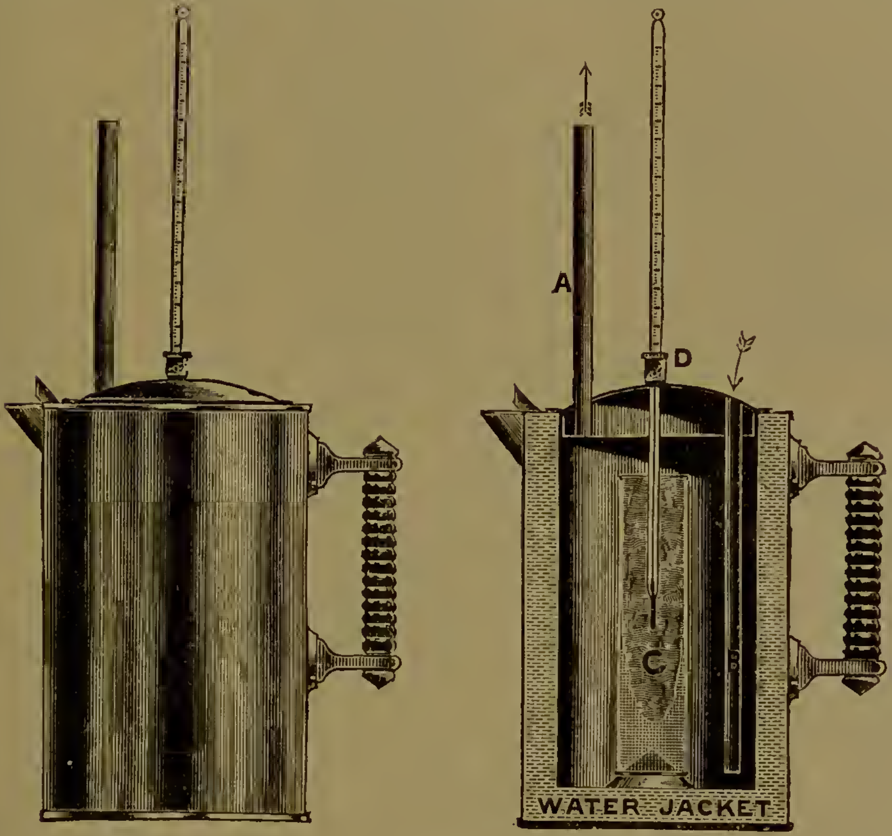

Fig. 68.

The following table contains the results of a number of experiments carried out by *Mackey* :[1]—

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[1] *Journ. Soc. Chem. Ind.* 1896, 90. Similar but very rough experiments were made before him by Gellatly (1874) to test the liability to spontaneous combustion of lubricating oils. Cp. also Kissling, *Journ. Soc. Chem. Ind.* 1895, 479.

No.	Substance.	Temperature in 1 hr.	Temperature in 1 hr. 15 m.	Temperature in 1 hr. 30 m.	Temperature in 2 hrs.	Maximum.		
		°C. = °F.	°C. = °F.	°C. = °F.	°C. = °F.	°C. = °F.	H.	M.
1	Cotton seed oil[1]	125=257	242=468	.. ..	.. ..	242=468	1	1
2	,, ,,	121=250	242=468	282=540	.. ..	284=543	1	35
3	,, ,,	128=262	212=414	225=437	.. ..	225=437	1	30
4	,, ,,	124=255	210=410	.. ..	.. ..	248=478	1	35
5	,, ,,	116=241	192=378	200=392	.. ..	200=392	1	30
6	,, ,,	118=244	191=376	202=396	.. ..	202=396	1	30
7	,, ,,	117=243	190=374	194=381	.. ..	194=381	1	[illegible]
8	,, ,,	112=234	177=351	204=399	.. ..	211=412	1	[illegible]
9	Olive oil fatty acids	114=237	177=351	.. ..	.. ..	196=385	1	[illegible]
10	,, ,,	105=221	165=329	.. ..	.. ..	293=559	1	[illegible]
11	,, ,,	102=216	135=275	208=406	.. ..	226=439	1	[illegible]
12	White Australian Oleine	103=217	115=239	191=376	.. ..	230=446	1	[illegible]
13	Olive oil (containing 1% free fatty acids)	98=208	102=216	104=219	.. ..	241=466	3	[illegible]
14	Oleine	98=208	101=214	102=216	.. ..	110=230	2	[illegible]
15	97% Oleine	98=208	100=212	102=216	.. ..	172=342	3	[illegible]
16	Belgian Oleine	98=208	99=210	100=212	.. ..	173=343	3	[illegible]
17	Olive oil (neutral)	98=208	100=212	101=214	.. ..	235=455	5	[illegible]
18	,, ,,	97=207	100=212	101=214	.. ..	228=442	4	[illegible]
19	,, ,,	97=207	.. ..	101=214	.. ..	235=455	4	55
20	Cotton seed oil	139=282	.. ..	.. ..	.. ..	200=392	1	4
21	Olive oil	99=210	101=214	102=216	103=217	113=235	4	30
22	Mixture of 50% of No. 20 and 50% of No. 21	102=216	117=243	.. ..	.. ..	200=392	1	[illegible]
23	,, 25 ,, ,, 75 ,,	99=210	105=221	112=234	.. ..	200=392	1	[illegible]
24	,, 10 ,, ,, 90 ,,	99=210	102=216	105=221	127=261	200=392	[illegible]	9

The method described being a comparative one,[2] the directions given must be strictly followed. It will be found useful before examining a sample, to test pure olive and cotton seed oils as representatives of a safe oil and a dangerous oil respectively.

I have worked with this "Cloth Oil Tester," and can recommend it as a very useful instrument. Less simple is the apparatus described by *Richards*.[3] This consists of an outer shell formed by a six-inch wrought-iron tube, closed at each end by removable discs of wood. Into this tube is inserted an inner four-inch tube of sheet-iron, with overlapping metal covers at each end. Thus there is left an air space of one inch round the inner tube and of three inches at each end. The apparatus is placed on a tripod and heated by a Bunsen burner. Three thermometers, which are inserted into the inner shell through the outer one, allow the temperature to be read off.

To test an oil, 50 grms. are evenly distributed over 50 grms. of cotton waste, the waste is carefully pushed into one end of the inner tube, and a thermometer inserted into the middle of the ball. A second ball of unoiled waste is placed similarly at the other end of the tube. On heating, the thermometer inserted into the blank waste should not rise above 100°-101° C.; this can be easily controlled by the reading of the middle thermometer. The latter should be kept at about 125° C. The results obtained with this apparatus are stated to have been useful for ascertaining the cause of fires and for gauging the degree of safety of oils. Furthermore, the percentage

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[1] Linseed oil and also maize oil would, of course, "fire" much sooner.

[2] In order to obtain more uniform results, *Archbutt* (*Journ. Soc. Chem. Ind.* 1899, 347) recommends the passing a regulated current of air, two litres per minute, through the apparatus (Fig. 68) down the tube B.

[3] *Journ. Soc. Chem. Ind.* 1892, 547.

of fatty oil which may be safely mixed with mineral oil was thus determined. The experiments showed that neat's foot oil and best lard oil may be mixed with mineral oil to the extent of 50-60 per cent, while in the case of cotton seed oil the limit of safety was reached at 25 per cent.

In the following table I collate a few analyses of some distilled oleines from "recovered grease," which are used as wool oils :—

Wool Oils—Distilled Oleines from Recovered Grease[1]

Flash Point.	Specific Gravity a 15·5° C.	Free Fatty Acids.	Unsaponifiable.	Neutral Wax.	Observer.
°F.		Per cent.	Per cent.	Per cent.	
...	0·8894	77·2[2]	26·8	...	Allen
...	0·9083	55·3[2]	35·9	11·6	,,
...	...	54·9[3]	34·5	11·28[4]	Lewkowitsch
338	0·9031	55·02	34·66	...	Hurst
342	0·8980	56·26	29·46	...	,,
322	0·9050	53·65	16·32	...	,,
...	0·9000	59·83	38·92	...	,,
...	0·9091	64·42	9·95	...	,,
415	0·941	...	41·7	...	Hess
...	0·9060 at 15°	41·5	57·7[5]	...	Marcusson

A few analyses of low-class wool oils, due to *Mackey*, are collated in the following table :—

Description.	Flash Point.	Moisture.	Unsaponifiable.
	°F.	Per cent.	Per cent.
Brown oleine, compound oil of English distilled and foreign oil	396	0·77	12·95
Brown foreign oleine, Belgian	354	0·75	18·69
Brown "oleine cloth oil," "manufactured"	349	0·64	25·58
"Black oil," recovered after using foreign and English distilled oleine (flannel district, Lancashire)	367	1·27	29·65
"Brown grease" recovered after using Gallipoli oil	419	1·07	29·77
Distilled oleine from brown grease and once recovered olive oil	342	0·77	37·19
"Black oil" recovered after using oleine and better class "cloth oils" (half "seek,"[6] half waste)	369	1·11	38·50
Brown oleine, distilled from brown grease	338	0·69	52·35
"Black oil," recovered after using recovered and low cloth oils (from waste)	331	0·67	67·30
"Brown pulling oil" (for rags), brown grease and hydrocarbons	374	0·74	78·25

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[1] Cp. chap. xi. p. 409, and chap. xvi.

[2] Calculated as oleic acid.

[3] Mean molecular weight 286.

[4] Consisting of 7·02 per cent of fatty acids and 4·26 per cent of combined alcohols.

[5] Consisting of 52·7 per cent of hydrocarbons and 5 per cent of alcohols.

[6] Cp. chap. xvi. "Seek Oil."

Emulsion wool oils are largely used on the Continent. They are prepared from neutral oils, oleic acid, and aqueous ammonia or an aqueous solution of sodium carbonate. They consist, therefore, of an emulsion of oil and soap solution.

In order to produce a more complete emulsion, gum or gelatin-like substances are occasionally added. They are detected by adding strong alcohol, which precipitates these substances. The following table (p. 961) contains the analyses of several emulsified oils :—

[TABLE

Emulsion Wool Oils

Name of Oil.	Na_2O. Per cent.	NH_3. Per cent.	Water. Per cent.	Fatty Matter. Per cent.	Fatty Acids Per cent.	Neutral Fat. Per cent.	Unsaponifiable. Per cent.	Soda Soap Anhydrous. Per cent.	Gummy Substances. Per cent.	Observer.
...	0·91	0·32	84·45	16·16	...	...	...	...	...	Horwitz[1]
...	...	...	76·67	20·86	...	...	...	0·91	0·72[2]	Morawski
"Patent oil"	0·41	1·36	...	...	70·8[3]	8·7	6·9	...	...	Lewkowitsch
...	...	12·50	34	...	45·0	7·0	...	1·5	..	Fuchs and Schiff

[1] *Journ. Soc. Chem. Ind.* 1890, 937. This paper contains many errors.

[2] This substance is most likely a decoction of Carrageen moss.

[3] Calculated as oleic acid.

The "Soluble Neoline" prepared according to Patent Specification 21976 November 17, 1893, belongs to this class of oils. From the proportions given in the specification I have calculated the following percentage composition:—

Water	56·18
Soap	8·40
Heavy paraffin oil	16·82
Potassium carbonate	4·55
Glycerin	14·05

To the class of emulsion wool oils belong also soap solutions prepared from castor oil or sulphonated castor oil, and a number of patented prescriptions, such as an emulsion of soap with wool fat,[1] or a solution of castor oil soda soap in oleine.[2]

B.—INDUSTRIES IN WHICH THE GLYCERIDES UNDERGO A CHEMICAL CHANGE, BUT ARE NOT SAPONIFIED

In these industries operations are carried out by means of which the glycerides undergo a more or less pronounced chemical change without, however, being broken up into their constituents—fatty acids and glycerol. These industries will be considered under the following heads:—

I. Pharmaceutical compounds.
II. Polymerised oils.
III. Boiled oils.
IV. Oxidised oils.
V. Vulcanised oils.
VI. Nitrated oils.
VII. Sulphonated oils, Turkey-red oils.

I. PHARMACEUTICAL COMPOUNDS

IODISED, BROMINATED, SULPHURISED OILS AND FATS

The oils belonging to this group have been recently introduced into pharmaceutical practice.

The assumption that the therapeutical effect of cod liver oil is due to the small amount of iodine it contains has led to the manufacture of *iodised* or *brominated* oils and fats. These are prepared by allowing oils and fats to absorb a certain amount of iodine or bromine. The method of preparing these oils and fats was at first carried out on the lines suggested by the iodine and bromine absorption methods described (chap. vi., p. 238), by treating the oils with iodo-chloride or bromine.[3] Later on gaseous hydrobromic or hydriodic acid[4] were substituted for the halogens themselves. The oils and fats selected for these preparations are sesamé oil, almond oil, and lard. At present there are found in commerce, the bromo-and iodo-compounds of sesamé oil under the name "Bromipin" and "Iodipin." The

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[1] Hutchinson, English Patent, 15,241, 1900.

[2] Sella, English Patent, 7491, 1901.

[3] German Patent, 96,495; E. Merck, *Zeit. ang. Chem.* 1898, 398.

[4] English Patent, 11,494, 1902; German Patent, 135,835; French Patent, 230,993 (W. Majert).

Bromipin is prepared in two strengths, viz. Bromipin containing 10 per cent of bromine, and Bromipin containing 33·3 per cent of bromine. Iodipin is also prepared in two strengths, viz. Iodipin containing 10 per cent of iodine, and Iodipin containing 25 per cent of iodine. As sesamé oil absorbs about 106-110 per cent of iodine, it is evident that the saturation of the doubly-linked carbon atoms has only taken place in a portion of the oil. For the glycerides of the fatty acids their methyl- and ethyl-esters have been substituted recently.

The taste of these compounds appears to have been found objectionable, since a patent has been taken out for the conversion of the iodised and brominated oils into a powder by mixing them with casein and milk sugar.[1]

Latterly, even *sulphurised* compounds are being manufactured on the lines of the sulphur chloride method described in Chapter VII. p. 302. The sulphurised fats are prepared by saponifying an oil or fat in the usual manner, liberating the fatty acids, and converting them into their ethylic and methylic esters.[2] These are then dissolved in carbon tetrachloride, and sulphur chloride is added (cp. also "Vulcanised Oils," p. 994). The product is washed with water and sodium carbonate solution, then again with water, whereupon the carbon tetrachloride is distilled off, and the residue washed again thoroughly with dilute caustic soda or a solution of sodium sulphide, and finally washed with water. A product thus obtained contained 6·4 per cent of sulphur. By the combined action of halogens and of sulphur compounds on sesamé oil, a preparation containing both iodised and sulphurised compounds is manufactured.[3] According to the patent specification, sesamé oil or poppy seed oil is treated with a solution of iodine in benzene; into this solution hydrogen sulphide is passed. Thus products containing from 10 to 30 per cent of iodine and about 2 per cent of sulphur are obtained.

II. POLYMERISED OILS—LITHOGRAPHIC VARNISHES

Under the term "polymerised oils" I comprise those products which are obtained by heating suitable oils to a somewhat elevated temperature. The chemical changes which occur are not yet fully understood; in the absence of a satisfactory explanation, they may, therefore, be conveniently summarised under the term "polymerisation." Typical polymerised oils are obtained from (1) linseed oil, (2) tung oil, (3) safflower oil, (4) castor oil.

The behaviour of these oils at elevated temperatures differs so much that each oil must be considered separately.

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[1] English Patent, 1903, 3430.

[2] W. Majert, German Patent, 140,827.

[3] English Patent, 1901, 24,321; United States Patent, 696,900.

(1) POLYMERISED LINSEED OIL

Lithographic Varnishes

French—*Huile pour la taille douce.* German—*Lithographenfirnis.*

The commercial lithographic varnishes are prepared by heating linseed oil to 250° or to 300° C., according to the thickness of the "varnish" desired. Hence the commercial lithographic varnishes are known under the trade terms "thin varnish," "medium varnish," "strong varnish," "extra strong varnish," "thick varnish," etc. These oils find application in lithographic printing and in the preparation of printers' ink.

"*Burnt varnish*" is a fairly quick drying oil, which will form a strong skin in twenty-four to forty-eight hours at the ordinary temperature. It is obtained by heating raw linseed oil up to its flash point, and allowing it then to burn quietly, with constant stirring until the required consistence is reached.

The commercial lithographic varnishes are perfectly clear, transparent viscid liquids. The thickest varnishes no longer leave a grease-spot on paper. The thin and medium varnishes are but slightly darker than raw linseed oil. Oils prepared by boiling over fire exhibit frequently a more or less strongly marked green fluorescence.

The following table contains the results of an examination of several lithographic varnishes by *Leeds*,[1] to which, for the sake of comparison, the corresponding numbers for a raw linseed oil are added :—

Lithographic Varnishes prepared by Boiling over Fire (*Leeds*)

	Specific Gravity at 15° C.	Saponification Value.	Iodine Value.	Oxidised Acids.	Unsaponifiable Matter.	Free Acids calculated as Oleic Acid.
		Mgrms. KOH.	Per cent.	Per cent.	Per cent.	Per cent.
Raw linseed oil	0·9321	194·8	169·0	0·30	...	0·85
"Tint" varnish	0·9584	197·5	113·2	1·50	...	1·46
"Thin" varnish	0·9661	196·9	100·0	2·50	0·62	1·76
"Middle" varnish	0·9721	197·5	91·6	4·20	0·85	1·71
"Strong" varnish	0·9741	190·9	86·7	6·50	0·79	2·16
"Extra strong" varnish	0·9780	188·9	83·5	7·50	0·91	2·51
"Burnt" thin varnish	0·9675	195·5	92·7	0·85	1·35	6·93

The mixed fatty acids, derived from the raw linseed oil and the "varnishes," freed from the unsaponifiable matter, gave the following results :—

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[1] *Journ. Soc. Chem. Ind.* 1894, 203.

Mixed Fatty Acids from Lithographic Varnishes (*Leeds*)

	Specific Gravity at 15·5° C.	Solidifying Point. °C.	Melting Point. °C.	Neutralisation Value. Mgrms. KOH.	Mean Combining Weight.	Iodine Value.
Raw linseed oil . .	0·923	...	24-26·5	195·8	286·5	145·5
"Tint" varnish . .	0·941	15	20·5	...	...	118·3
"Thin" varnish . .	0·949	18	22	...	...	108·8
"Middle" varnish .	0·950	22	24	205·8	272·6	97·7
"Strong" varnish .	0·953	24	25·5	207·7	270·1	87·3
"Extra strong" varnish	0·955	23	27	207·9	269·8	90·8
"Burnt" thin varnish .	...	19	23	...	...	99·3

The chemical change which the linseed oil undergoes manifests itself in an increase of specific gravity, a decrease in the iodine absorption, and notably in a considerable decrease in the yield of hexabromide (*Lewkowitsch*[1]). This is illustrated by the following table, in which a typical linseed oil is contrasted with a linseed oil heated to 600° F., and with a number of commercial lithographic varnishes:—

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[1] *Analyst*, 1904, 2.

[TABLE

Polymerised Linseed Oils—Lithographic Varnishes (Lewkowitsch)

	Specific Gravity at 60° F.	Saponification Value.	Iodine Value.	Hexabromides.	Hehner Value.	Oxidised Fatty Acids.	Unsaponifiable Matter.	Glycerine obtained.	Acid Value.[1]	Acetyl Value.	Iodine Value of Fatty Acids.	Liquid Fatty Acids.[2]	Iodine Value of	
													Liquid[2] Acids.	Solid[2] Acids.
				Per cent.		Per cent.	Per cent.	Per cent.				Per cent.		
Linseed oil, raw .	0·9308	..	186·4	24·17										
Linseed oil, heated to 600° F. . . .	0·9354	...	176·3	8·44										
Thin varnish, No. I.	0·9676	189·5	107·7	0·17	94·75	4·17	1·76	9·71	6·09	6·5	114·74	39·31	131·29	106·2
,, ,, ,, II.	0·9691	193·0	125·3	2·00	94·8	0·34	0·13							
Medium ,, ,, I.	0·9693	194·4	121·9	0·95	93·8	1·48	0·57							
,, ,, ,, II.	0·9703	190·5	126·5	0·0	...	1·53	1·8							
Thick ,, ,, I.	0·9720	190·0	109·4	0·24	94·68	6·36	1·45	9·17	5·12	1·65	113·53	32·31	130·4	106·43
,, ,, ,, II.	0·9747	193·7	118·5	0·0	95·6	0·36	0·25							
Burnt ,, . .	0·9912	178·6	102·69	0·0	93·53	9·12	1·14							

[1] There was no colophony present.

[2] By lead-salt-ether method.

The numbers recorded in the foregoing tables show in a general way (considering that we have to deal with commercial products) that the glyceridic part of the oil has not undergone destruction, and that the higher the temperature to which the heating is carried, the greater becomes the specific gravity. Apparently the amount of oxidised acids seems also to increase in proportion to the specific gravity. The irregularities in their percentage numbers prove, however, that the proportion of oxidised acids depends on the access of air during the boiling, and the conclusion must therefore be drawn that, if access of air be excluded entirely, practically no oxidised acids would be formed. The numbers given in the column "hexabromides" show that during the process of heating, the linolenic acids become polymerised first. The considerable iodine values which the lithographic varnishes still exhibit may then be explained by the glycerides of linolic acid having remained intact to a large extent. Thus the hexabromide test becomes of importance (in addition to the specific gravity test) in the differentiation of lithographic varnishes from linseed oil.[1]

The drying power of linseed oil diminishes with the rise of the temperature in the boiling process. Thus, whereas "thin" lithographic varnishes dry approximately as well as raw linseed oil does, the "extra strong" varnish and burnt varnish dry only very slowly at the ordinary temperature.

(2) POLYMERISED TUNG OIL

It has been shown above (chap. xiv. p. 460) that on heating tung oil to 180° C. for two hours, or to 250° C. for a short time, a jelly-like mass is produced. As this product is obtained whilst air is excluded, its formation must, pending a better explanation, be ascribed to polymerisation. On standing, this mass becomes so solid that it can be powdered. The examination of a powdered mass prepared in my laboratory led to the following result, which I contrast with the corresponding numbers of the original oil:—

Polymerised Tung Oil (Lewkowitsch).

	Saponification Value.	Iodine Value.
Original tung oil	193	163
Polymerised tung oil	205·2	107·7

A satisfactory technical application of polymerised tung oil has not been found yet, although its semi-elastic properties, and its apparent resistance to air, moisture, etc., suggest its employment as a substitute for solidified linseed oil (p. 991). A number of patents[2]

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[1] *Analyst*, 1904, 2.

[2] Cp. Kronstein, English Patent, 17,378, 1900; 1386, 1901; 1387, 1901; 2679, 1901.

have been taken out for processes purporting to produce varnishes (mixtures of polymerised tung oil with gum-resins) from polymerised tung oil alone, or from mixtures of polymerised tung oil with linseed oil. Recently a patent[1] has been taken out for the manufacture of linoleum from polymerised tung oil and solidified linseed oil.

(3) Polymerised Safflower Oil

The pronounced drying properties of safflower oil rendered it likely that this oil also would become polymerised under the same conditions as linseed oil. Experiments carried out in my laboratory have proved this to be the case. The numbers so obtained are given in the following table, in which the original safflower oil is contrasted with its polymerisation products, and with the native product "roghan" (Afridi wax), the manufacture of which has been described in Chapter XIV. p. 483 :—

	Specific Gravity.	Iodine Value.
Safflower oil	0·9274	147·3
,, ,, heated to 300° C. for 2 hours .	0·92938	143·4
,, ,, ,, ,, 4 ,, .	0·93077	142·7
,, ,, ,, ,, 6 ,, .	0·93949	121·7
,, ,, burnt, 6 minutes . . .	0·95481	99·3
,, ,, Indian distilled oil ("roghan," Afridi wax)	0·9638	121·8

(4) Polymerised Castor Oil

The changes which castor oil undergoes on being subjected to destructive distillation have been described already (p. 649). It has further been shown that if the distillation of castor oil be stopped just before the mass is converted into an indiarubber-like substance, the oily residue still contains glycerides.

With a view to more closely following the changes which castor oil undergoes, I have heated the oil rapidly to 200°, 250°, 300°, and 350° C. in an open dish and determined the iodine values of the products.

Polymerisation of Castor Oil on Heating (*Lewkowitsch*).

	Iodine Value.
Original castor oil	83·0
,, ,, after heating rapidly to 200° C. .	87·03
,, ,, ,, ,, 250° C. .	89·28
,, ,, ,, ,, 300° C. .	90·19
,, ,, ,, ,, 350° C. .	93·72

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[1] English Patent 5789, 1903, Dewar and Linoleum Manufacturing Co.

Fendler[1] quite recently examined the product obtained on a large scale by heating castor oil in a retort, so that the temperature reached after one hour 300° C. The product obtained had the following characteristics:—

Specific gravity at 15° C.	0·9505
Saponification value	191·8
Iodine value	101·0
Acetyl value	67·4

From the iodine number it follows that the polymerisation has not affected the unsaturated carbon atoms. The increase in the iodine values, and the considerable decrease of the acetyl value, as contrasted with the original castor oil, prove that the polymerisation has taken place in the first instance in the direction of the formation of glycerides of di-, tri-, tetra-, and penta-ricinoleic acids, which in their turn became converted into the glyceride of triundecylenic acid (cp. Turkey-red oil, chap. xv.).

The product examined by *Fendler* is manufactured on a commercial scale[2] by heating castor oil to 300° C., until about 5 per cent of its weight has distilled over. It differs from the original castor oil in that it is almost insoluble in absolute alcohol, as also in 90 per cent alcohol and acetic acid, whereas it is miscible with mineral oils in every proportion, and forms an emulsion with water. These emulsions separate, however, after a short time into two layers. The product is most likely a mixture of glycerides of undecylenic acid (see p. 649) and glycerides of polymerised ricinoleic acids.

Another method of converting castor oil into a polymerised product consists in treating castor oil with a concentrated solution of zinc chloride,[3] or the fused hydrated crystallised salt. The product obtained is a horny mass, which may be freed from zinc chloride by washing with water. The degree of solidification (polymerisation) depends on the proportion of zinc chloride used, its concentration, and the temperature employed. This product was proposed to be used as a covering and insulating mass. Very likely it is identical with the elastic, horny mass left in a retort on heating castor oil until the residue is suddenly converted into the solid mass, described p. 649.

Hitherto this product does not appear to have been employed in the arts.

III. BOILED OILS

French—*Huile cuite.* German—*Gekochtes Leinöl, Leinölfirnis.*

The oils described under this head take their name from the almost obsolete process of heating linseed oil, mixed with a small

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[1] *Berichte d. d. pharm. Gesellschaft*, 1904, 135.

[2] German Patent 104,499, Chemische Fabrik Flörsheim, Dr. H. Nördlinger; it is sold under the fancy name "Floricin."

[3] C. R. Alder Wright, *Journ. Soc. Chem. Ind.* 1887, 326.

quantity of suitable metallic oxides or metallic salts—*driers, siccatives*—over free fire to temperatures varying from 210° to 260° C.

This process was termed "oil boiling." Up till recently this industry had remained a truly empirical industry, and was carried on much in the same fashion as it was practised by its inventor, the Dutch painter *Van Eyck*. It was found that linseed oil, after heating with lead oxide, absorbed oxygen more rapidly than linseed oil not so prepared, so that whereas raw linseed oil requires about three days for drying to an elastic skin, the drying process is so much accelerated by the treatment over free fire that linseed oil will dry even within six to eight hours to an elastic skin.

What action takes place during the process of boiling is not yet fully known. A slight decomposition of the glycerides undoubtedly takes place, as is proved by the evolution of acroleïn vapours during the boiling; but such decomposition of the linseed oil is very limited, as the "boiled oil," like the polymerised linseed oils (lithographic varnish), still yields almost its full amount of glycerol. Moreover, practical experience has proved that boiled oils must contain glycerides, since "boiled oils" cannot be obtained from linseed oil fatty acids, or ethylic esters of the mixed linseed oil fatty acids.[1]

Whilst the oil is under the influence of the high temperature, polymerisation will occur to some extent (see p. 967). No hydrocarbons (due to destructive distillation) are formed, or, at any rate, not to an appreciable extent, as has been proved by the small amounts of unsaponifiable matter found in commercial boiled oils (cp. table, p. 977).

For a long time the view was held that oxidation of the oil takes place, although even in the antiquated process of boiling over free fire, the oil is kept covered and almost wholly protected from contact with air. The explanation that the metallic oxides act as oxygen carriers during the process of boiling (an assumption which seemed to find support in the fact that a number of boiled oils had low iodine values) is equally unfounded. For from the numbers given below it will be seen that "boiled oils" can be prepared having iodine values which lie very little below those yielded by a normal raw linseed oil.

Since an oxidised oil is characterised by containing considerable amounts of oxidised acids, whereas the proportion of such acids in the boiled oils is but insignificant, the view must at present be accepted that the "boiled oils" have undergone a slight change only in their chemical composition.

The treatment with "driers" seems to be an empirical way of preparing metal salts (lead salts or manganese salts) of the fatty acids of the boiled oils, partial saponification of the glycerides taking place at the high temperature to which the oils are subjected whilst being boiled.

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[1] Cp. Henriques, *Zeit. f. ang. Chem.* 1898. 343.

These lead salts (or metal salts) of the fatty acids are able to act as oxygen carriers in the process of "drying," when the boiled oils are exposed, either in their original state or in admixture with pigments, gum-resins, etc., to the atmosphere (see p. 988).

These views find support in the modern methods of preparing "boiled oils."

Thus at present the bulk of the "boiled oils" is obtained by heating linseed oil with driers to a temperature of about 150° C. only.

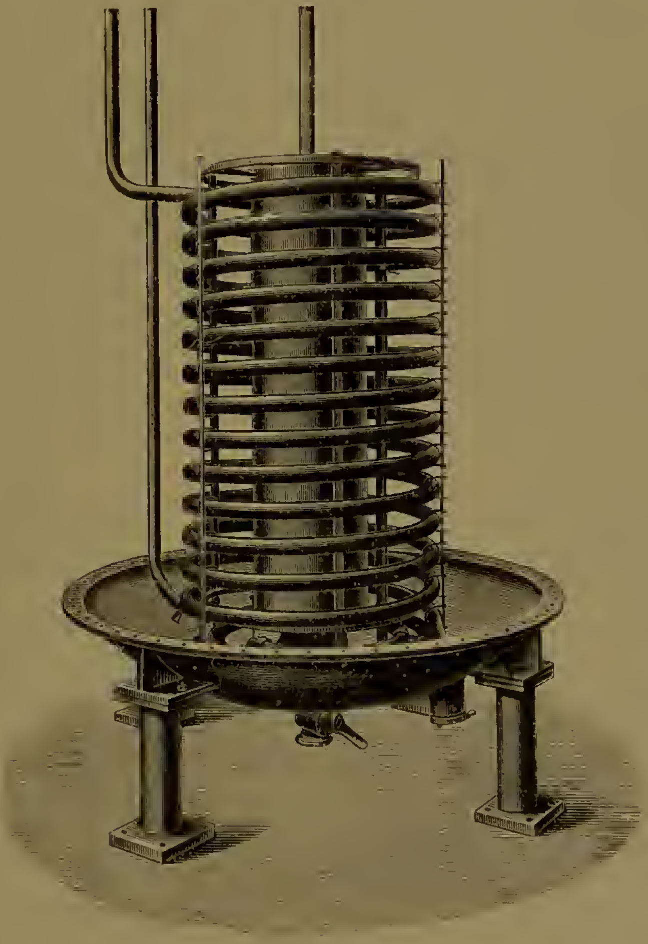

Fig. 69.

The process is carried out by introducing the oil into a cylindrical vessel provided with a heating coil and an agitating gear, so as to produce an intimate intermixture between oil and drier whilst they are heated to the desired temperature. The internal arrangement of a modern oil-boiling vessel[1] is illustrated by Fig. 69, the cylindrical part of the vessel having been removed to show the heating coils and the stirring apparatus.

According to the quality and amount of drier added, and the

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[1] I am indebted to Messrs. Manlove, Alliott, and Co., Limited, Nottingham, for this illustration.

length of time during which the oil is heated ("boiled"), pale or dark oils are produced. The former are known in commerce as "pale boiled oils," the latter as "double boiled oils." The temperature can be reduced even to 120° C. by merely dissolving "liquid driers" (solutions of lead linoleate, etc., in linseed oil), and assisting the operation, if required, by a current of air.[1]

This last process yields somewhat inferior drying oils than are obtained by boiling at 150° C. with lead oxide, etc. It may, however, be inferred therefrom that in order to obtain a quickly drying oil it suffices to prepare a solution of metal salts in oil, etc.

This view has even led to the preparation of "boiled oils" in the cold, by merely adding a solution of lead linoleate or manganese linoleate to linseed oil and carefully intermixing with the oil. (An oil having the properties of a "boiled" oil can also be prepared by carefully grinding linseed oil with manganese borate in the cold.) Yet, there is no doubt that the oils prepared in the cold have inferior drying properties, as compared with those obtained at a higher temperature. From this it would follow that a certain amount of polymerisation must take place to accelerate the subsequent oxidation, when the oil is allowed to "dry."

The suitability of a raw linseed oil for making "boiled oil" was hitherto determined in practice by its age. It is well known that fresh oils ("green" oils) give a scum on boiling, and effervesce strongly, whereas old "tanked" oils, from which water and "mucilage" have settled out on storing or "tanking," were found to yield the best boiled oil. The practical test for suitability is to heat the oil rapidly in a test tube to about 300° C. A suitable oil remains clear, whereas a "green" oil, or an insufficiently refined oil, would show "mucilage" (cp. chap. xiv., p. 453). The observations made by *Thompson* (p. 453) prove that the "mucilage" is due to the presence of inorganic salts, which separate out from the "tanked" oil, carrying down with them organic impurities left in the oil. Further proof for the correctness of this view is given by the fact that these impurities are removed by refining raw linseed oil. Other tests for purity have been given already under the heading "Linseed Oil" (p. 457). Practical experience has shown that Baltic oil is better for the manufacture of boiled oil than Indian oil; this is explained by the greater purity of the Baltic seed. Cold pressed linseed oil is better than hot pressed oil; this finds its explanation in the fact that the cold pressed oils contain smaller amounts of solid glycerides than the hot pressed oils.

With a view to removing the bulk of the solid glycerides from linseed oil, as they obviously impede the drying property of the oil, I have tried on a large scale to separate the solid glycerides by the process of "demargarination," viz. by cooling the linseed oil to −25°.

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[1] Cp. Hartley and Blenkinsop, English Patent 11,629, 1890.

This process (for which a provisional patent only was taken) has been abandoned as unremunerative.[1]

Linseed oil is practically the only oil that is used in the manufacture of boiled oils on the large scale. Other vegetable drying oils—like candle nut oil, safflower oil (cp. table, p. 976)—also furnish boiled oils, but their drying properties are not so good as those of boiled linseed oil. Fish and blubber oils seem to be unsuitable for the preparation of boiled oils. The statements made in specifications as to the usefulness of these oils, either as such or in admixture with linseed oil, must therefore be accepted with reserve.

Driers.[2]—In the older processes only the metallic oxides of lead and manganese or their inorganic salts, such as litharge, red lead, manganese dioxide, were used as driers; zinc,[3] copper, and iron salts being incapable of imparting to the oils the desired properties. More recently acetate, oxalate, and borate of manganese are being employed. Since rosin is capable of absorbing oxygen from the air, the metallic salts of the rosin acids[4] have also come into vogue as driers.

Their metallic salts are either prepared by precipitation of a (soda) soap solution by means of salts, *e.g.* sodium rosinate by manganese sulphate, or are simply synthetised by fusing together a metallic oxide with colophony; hence there are discerned in commerce "precipitated" driers and "fused" driers.

By precipitating rosin soap solutions, or fusing colophony, as the case may be, with mixed manganese and lead salts, "precipitated" or "fused" *mangano-lead driers* are obtained.

A good method to distinguish "precipitated" driers from "fused" driers is afforded by the determination of water. Only the "precipitated" driers contain notable quantities of moisture (up to 6 per cent).

A further development in the industry of driers was reached by the employment of the metallic salts of linseed oil fatty acids. These salts are prepared either by precipitating soap solutions, obtained by saponifying linseed oil, with metallic salts, or by heating the fatty acids together with oxides. Thus "precipitated" manganese linoleate and lead linoleate or the "fused" salts are obtained. By means of such methods the writer prepared driers from *tung oil.* Thus a lead tungate, manganese tungate, or a mixture of the two—lead-mangano tungate—were manufactured on the large scale. The driers prepared from linseed oil fatty acids, tung oil fatty acids, and colophony are soluble in oil of turps (turpentine oil), ether, chloroform, and linseed oil,[5] and are therefore termed "soluble driers."

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[1] Cp. Lewkowitsch, *Jahrbuch der Chemie*, xii. 370. The same process has been patented by Hertkorn, German Patents 129,809, 137,306.

[2] Cp. Weger, *Zeit. f. ang. Chem.* 1896, 531; 1897, 401, 542, 560.

[3] Cp. *Thorp*, *Technology Quart.* 3, 9.

[4] With regard to driers from copals—"copal resinates"—cp. Bottler, *Dingl. Polyt. Journ.* 1898, 70.

[5] It should be noted that the solubility of "linoleates" and rosinates in ether or chloroform in the cold exactly coincides with their solubility in linseed oil at somewhat elevated temperatures—up to 120° C. Cp. Lippert, *Zeit. f. ang. Chem.* 1903, 366.

Solutions of these driers in linseed oil or in turpentine oil or in a mixture of both are obtainable in commerce under the names "liquid driers," "terebene,"[1] and other fancy names.

The examination of driers consisting of metallic oxides or of metallic salts of inorganic acids is carried out by the well-known methods of mineral analysis.[2] The valuation of the "soluble driers" cannot be based on the proportion of the metal, as determined by incineration, inasmuch as the oxides held in suspension, and therefore not chemically combined with fatty acids or rosin acids, are not only useless to the manufacturer of boiled oil, but even injurious, as they render the oil turbid. A preliminary test consists in treating the drier with organic solvents. A good drier should dissolve completely in ether, or, in the case of lead rosinate, in chloroform and in oil of turps. (Turpentine oil also dissolves lead rosinate, but the dissolved drier separates out.)

In the analytical examination of a soluble drier the organic matter is first burnt off in a porcelain crucible, and the amount of lead, manganese, etc., is determined in the ash. The weight of the ash does not always give useful indications, as the fused driers often contain sand, etc. In addition to lead and manganese, the calcium in the ash may be determined. (Calcium rosinate is a legitimate constituent of driers.) A fresh portion of the sample is then extracted with ether or chloroform or oil of turps. From the filtered solution the solvent is evaporated off and the residue incinerated. In the ash, the lead or manganese, or both (as the case may be), are determined quantitatively, and the difference between the manganese found in this experiment and that found in the first experiment corresponds to the amount of manganese present as soluble drier. The result may be checked by determining the dissolved manganese in an aliquot portion of the solution. In the case of a rosinate the dissolved lead must be determined by difference, as the chloroform is stated to be only driven off completely from the rosinate at a red heat, when a portion of the lead also volatilises as chloride.

The fatty acids or rosin acids, although their examination is of minor importance, may be determined by decomposing the ethereal solution with mineral acid. It must, however, be understood that the results of a chemical analysis alone are not sufficient to furnish the data on which an opinion as to the properties the drier will impart to the oil can be based. The colour of the boiled oil to be prepared, its drying power, and other conditions, greatly influence the choice and quantity of the solvent.

A table detailing the proportions of metal contained in some commercial driers, as also the minimum temperatures at which they may be used, is given in my *Laboratory Companion to the Fats and Oils Industries*.[3]

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[1] Cp. Fawsitt, *Journ. Soc. Chem. Ind.* 1903, 538.

[2] With regard to the analysis of manganese borate, cp. Endemann and Paisley, *Amer. Chem. Journ.* 1903, 68.

[3] Table No. 43, p. 84.

Each manufacturer appears to have his own "formula" for the quantity and composition of driers he adds to the oil in the boiling process. These "formulæ" are considered valuable secrets. As a rule, a quantity of driers not exceeding 2 to 3 per cent of the oil is added. The best results are stated by *Weger* to be obtained by using a mangano-lead drier, the manganese and lead salts being mixed in such proportions that the metallic lead (Pb) and metallic manganese (Mn) are present in the proportion of 5 to 1. The solid driers suffer from the drawback that a considerable amount of "foots" settles out from the stored finished product. No such deposit is formed when liquid driers are employed.

The drying power of finished boiled oil depends up to a certain limit only on the quantity of drier added. After a certain amount of drier has been incorporated with the oil, its drying power is not increased by a further addition of drier; in some cases the drying power actually decreases. Thus *Weger* states that the shortest time necessary for drying to an elastic skin is reached when the boiled oil contains 0·2 per cent of manganese as metal, and in the case of mangano-lead driers 0·6 per cent of metals, the proportion of lead to manganese being 5 to 1.[1]

The chemical examination of boiled oils embraces the detection of adulterants, such as fish oils, vegetable oils (other than linseed oil), mineral oils, rosin oils, and rosin (cp. "Linseed Oil," p. 457). Oils prepared with liquid driers may legitimately contain small proportions of oil of turpentine. The so-called patent boiled oils are, as a rule, adulterated oils.

Boiled oil is readily differentiated from raw oil by the specific gravity test, by the presence of drier (giving a residue on incineration), and by the hexabromide test (see below). Boiled oil is frequently mixed with raw linseed oil, since boiled oil, if used alone, gives in some cases a "hard" coat liable to crack; hence the detection of raw linseed oil in boiled oils is of little practical importance in this country.

In those countries, however, where raw linseed oil and boiled oil are assessed differently by the custom-house officials, the rapid distinction of linseed oil from boiled oil is frequently required. *Finkener* recommends, for custom-house purposes, the following test, by which 25 per cent of boiled oil can be detected in raw oil. The following reagents are required:—A 20 per cent ammonia solution, and a solution containing 100 grms. of lead acetate and 32 grms. of glycerin in 120 c.c. of water. The test is carried out as follows:—1 c.c. of the ammonia solution is mixed with 5 c.c. of the lead solution, 12 c.c. of the sample are added, and the whole is vigorously shaken together and then heated for three minutes to 100° C. If the sample be pure linseed oil it will form two layers on standing,

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[1] *Zeit. f. ang. Chem.* 1897, 401, 524, 560; *Die Sauerstoffaufnahme der Oele und Harze*, E. Baldamus, Leipzig (cp. Lippert, *Zeit. f. ang. Chem.* 1897, 655; 1898, 412. 431; 1903, 366.

the lower one being clear, while if the sample contain boiled oil it will set to a soft, viscous mass.

The best test for the detection and approximate determination of raw linseed oil in boiled oils prepared at elevated temperatures is the hexabromide test.[1] The oils boiled over free fire by the old process undergo polymerisation much in the same way as the polymerised oils (p. 963). It has been shown above that the yield of hexabromides rapidly decreases with the temperature employed. Hence these boiled oils will give a much lower yield of hexabromides. In boiled oils, however, which have not been heated to such high temperatures this test does not appear to give a decisive answer, as the oils, not having undergone polymerisation, still yield approximately the same amounts of hexabromides as do the original oils.

This is clearly brought out by the following table, in which the iodine value of some "pale boiled" oils and some "double boiled" oils prepared at 150° C. are recorded. There is a considerable decrease in the yield of hexabromides coincident with the corresponding, although by no means proportionate, decrease of the iodine value. My view that these decreases are due to polymerisation which has taken place in consequence of the high temperature is borne out by the last three oils, prepared by an ozone process examined by me. The treatment was carried out at temperatures, at which polymerisation does not take place; hence the yield of hexabromides, as also the iodine value, is little lower than that of the original oil.

Characteristics of Boiled Oils (*Lewkowitsch*)

Name.	Specific Gravity.	Iodine Value.	Hexabromides from Glycerides.
			Per cent.
Linseed oil (raw)	0·9308	186·4	24·17
Pale boiled linseed oil	0·9429	171·0	20·97
Double ,, ,, ,,	0·9449	169·96	13·03
Ozonised ,, ,,	0·9310	180·1	36·26-36·34
,, ,, ,,	0·9388	171·2	25·73
,, ,, ,,	0·9483	169·7	30·19
Safflower oil (raw)	0·92461	146·46	traces
Double boiled safflower oil	0·9340	137·3	
Pale ,, ,, ,,	0·9360	139·1	
,, ,, ,, ,,	0·93613	137·0	
Double ,, ,, ,,	0·9447	141·8	none
,, ,, ,, ,,	0·95035	127·3	

The amount of oxidised acids in boiled oils should be low, and should not much exceed the proportions stated above (table, p. 966) for lithographic varnishes. *Fahrion* has drawn the conclusion (from a few experiments) that a boiled oil is the better the less oxidised acids it contains (cp. p. 989).

In the chemical examination of a boiled oil the numbers, collated in the following table, may be found useful:—

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[1] Lewkowitsch, *Analyst*, 1904, 2.

Some Constants and Variables of Commercial Boiled Oils

Description.	Specific Gravity at 15·5° C.	Acid Value.	Saponification Value.	Hehner Value.	Iodine Value.	Unsaponifiable.	Oxidised Acids.	Observer.
				Per cent.	Per cent.	Per cent.	Per cent.	
Somewhat thin and fluid	...	13·4	...	...	101·3	...	0·5	Fahrion
Very viscid	...	24·9	...	...	77·3	...	4·1	,,
Tacky, yielding strings	...	32·6	...	...	73·7	...	7·6	,,
...	...	...	188·1-192	92-92·3 (2 samples)	145·1-157·2	0·3-0·72	...	Ulzer
...	...	...	...	...	149·7-153·4	...	...	Wild
...	...	...	...	...	...	0·43-1·71	...	Bach
Very thin	0·947	8·85	182·2	...	...	2·34	...	Williams
Thin	0·948	7·06	180·9	...	...	1·27	...	,,
Thin	0·961	12·43	179·5	...	...	2·11	...	,,
Stout	0·972	19·69	189·3	...	...	2·01	...	,,
Stout	0·982	20·89	185·6	...	...	2·04	...	,,
Very Stout	0·983	24·97	183·0	...	...	2·14	...	,,
Solid	...	14·02	193·9	...	...	2·08	...	,,
Varying in consistence in the same order, from thin to very viscous	...	4·8	188·7	...	159·0	...	...	Kitt
	...	5·2	189·1	...	100·7	...	...	,,
	...	7·8	189·1	...	95·6	...	...	,,
	...	9·5	186·6	...	83·6	...	...	,,
	...	9·1	187·2	...	79·1	...	...	,,
	...	11·7	187·2	...	76·2	...	...	,,
	...	18·8	192·3	...	71·1	...	...	,,
Double boiled oil	0·9493	...	191·0	...	161·0	1·9	...	Lewkowitsch
Commercial boiled oils, 8 samples	0·9355-0·9474	2·8-6·4	187·5-192·2	...	180·4-183·3	1·12	...	McIlhiney

It should be noted that, owing to the presence of metals in boiled oils, the determination of the iodine value will lead to too high results, unless the metal be first removed by treatment with mineral acids. The error that may be committed by not following these directions is shown by the figures contained in the following table:—

Iodine Values of Boiled Oils (*Lewkowitsch*)

Boiled Oil from	In Original Oil.	In Oil after Removal of Metal.
Linseed oil . .	173·3	169·7
,, ,, . .	177·2	171·1
Safflower oil . .	134·9	130·7

The valuation of a boiled oil which has been found free from adulterants must be based on "practical" tests, by exposing the oil in a thin layer on glass plates to the action of the atmosphere in the manner described on page 311, and under "Linseed Oil," p. 457. The oil is exposed either in its original state or after admixture with pigments, such as are used in the preparation of paints. A weighed or measured amount of boiled oil is therefore intimately intermixed with a weighed amount of pigment, the mass is spread in a thin layer on a glass plate, and exposed to the atmosphere side by side with a boiled oil of known quality. A good deal of practical experience is, however, required to arrive at a definite opinion as to the value of a boiled oil.[1]

Boiled oil is extensively used in the preparation of **paints** and **varnishes.**

The examination of **paints** has been briefly sketched out already. The paint is shaken out with ether; a mineral acid is added to decompose soap and to bring the pigment into solution, in case it be soluble in acid. The ethereal layer is separated from the aqueous solution and any undissolved pigment. After evaporating off the ether the residual oil may be subjected to further examination. The mineral matter is examined by the well-known methods of inorganic analysis.

The examination of paints as regards their suitability for withstanding the action of the atmosphere falls outside the scope of this work.

The **varnishes—oil varnishes**—consist of a mixture of boiled oil, various gum-resins, and oil of turps.

The manufacture of varnishes is guarded as a valuable trade secret, the "art" of the manufacturer consisting in the suitable selection of gum-resins and preparing them for "running" with oil. Most of the gum-resins must be subjected to a preliminary treatment by heating to a temperature of above 300° C. They are thereby

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[1] Cp. Weger's papers referred to, p. 975; Lippert, *Zeit. f. ang. Chem.* 1900, 134; 1903, 366.

fused and undergo a kind of destructive distillation; owing to an oily portion distilling over they lose from 5 to 25 per cent of their weight. The attempts that have been made hitherto to avoid this loss by dissolving the gums previous to mixing with oil in oil of turps, or dissolving them in linseed oil under pressure[1] have not been successful. In practice the fused gums are dissolved in the hot in a drying oil or in a boiled oil; in the former case the oil is "boiled" after suitable driers have been added. The product so obtained is termed "varnish oil." The varnish oil is allowed to settle out, so that "foots" may separate or is filtered through a filter press. The varnish oil is then diluted or "thinned" with oil of turps to produce the commercial varnish.

The most suitable oil, and practically the only one used for high class varnishes, is linseed oil. A large number of patents have been taken out purporting to successfully substitute linseed oil by tung oil, or by mixtures of linseed oil and tung oil. In most of the products of this kind which the author has examined, the expensive gums were substituted by colophony. With regard to the oxygen absorption power of colophony, cp. Table No. 38 of the *Laboratory Companion to the Fats and Oils Industries.*

The oil of turps is also being substituted by cheaper hydrocarbons, especially petroleum hydrocarbons of the same boiling point.

A complete chemical analysis of varnishes is in the present state of our knowledge an extremely difficult problem. Whilst the fatty oil may be more or less readily recognised, it is in some cases impossible to identify the gum constituent by chemical means alone, considerable practical experience being required to supplement the purely chemical examination.

The first object in the chemical examination of a varnish is to remove the volatile solvent. This is done by treating 100 grms. of the varnish in a current of steam[2] until no more volatile oil comes over with the vapours. The examination of the volatile oil is comparatively simple. The specific gravity, the boiling point, and also the iodine value of the sample, will afford the necessary guidance. It may be added that the iodine value of genuine oil of turps is from 350 to 400.

The residue left in the flask is then freed from water. By ascertaining the amount of glycerin it yields on saponification, the proportion of boiled oil can be arrived at approximately. The separation of the gums from the boiled oil cannot always be carried out satisfactorily. The usual characteristics (constants and variables) of gums do not lead to decisive information, for it must be borne in mind that the gums are heated to about 300° C., so that their chemical composition becomes entirely changed. *Lewkowitsch*[3] examined a number of gums used in the manufacture of varnishes after heating them to 300° C. The numbers given in the following table may serve as a guide in the analysis of varnishes:—

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[1] Smith, *Journ. Soc. Chem. Ind.* 1901, 1076. Lewkowitsch, *ibid.* 1901, 1077. Lippert, *Chem. Rev.* 1901, 177.

[2] Cp. M'Ilhiney, *Journ. Amer. Chem. Soc.* 1895, 344.

[3] *Analyst*, 1901, 37.

Some Constants and Variables of Gum-Resins used in Varnishes (Lewkowitsch)

	Original Gum-Resins.						Gum-Resins after Heating to 300° C.				
	Acid Value.	Saponification Value.	Unsaponifiable. Per cent.	Iodine Value.		Soluble in Alcohol. Per cent.	Acid Value.	Saponification Value.	Unsaponifiable. Per cent.	Iodine Value.	
				By ICl. Addition.	By Bromine Addition.					By ICl. Addition.	By Bromine Addition.
Copal, Commercial	109·8	143·1	7·96	135·5	183·6	93·06	26·49	85·4	14·73	124·3	181·3
Copal, Commercial	42·43	66·82	14·99	191·2	114·6	54·83	24·94	61·04	46·40	143·7	233·5
Copal, Sierra Leone	72·83	119·03	18·81	105·7	96·05	...	12·89	114·9	17·22	125·5	173·6
Copal, Manila	127·6	175·17	15·98	137·9	188·2	...	68·21	136·3	22·99	133·3	186·4
Copal, Brazil	108·99	171·4	7·66	127·7	72·66	...	46·25	113·8	38·74	136·7	225·9
Copal, Sierra Leone	65·7	110·5	16·27	94·55	117·0	...	15·32	123·8	22·31	95·23	135·4
Kauri	37·39	53·84	20·07	90·99	...	...	17·14	61·07	10·39	67·70	74·71
Mastic	52·73	81·79	51·13	175·7	185·0	84·41	23·23	50·24	49·28	165·0	217·8
Shellac, Dark	61·13	203·0	3·56	35·57	13·25						
Sandarac, Mogador	134·39	143·42	13·2	112·2	99·98	...	64·84	136·14	14·28	126·4	69·13
Sandarac, Australia	131·15	134·32	17·44	125·4	63·83	...	106·6	137·26	9·93		
Animi No. 1	18·69	73·15	6·3	105·3	182·7	...	9·25	58·73	...	106·1	207·4
Animi No. 2	30·22	93·5	6·85	96·21	95·85						
Dammar	35·22	32·73	75·96	127 5	169·4	...	10·85	60·44	86·57	127·0	196·8
Amber	16·7	121·27	18·86	58·98	82·82						
Succinit	11·24	113·68	7·06	55·05	78·4	...	10·60	99·19	16·25	74·34	147·8
Colophony	...	...	...	...	...	...	146·46	153·01	15·94	133·7	302·1

The examination of the ash will indicate what metal or metals have been used as driers. Considerable quantities of lime in the ash point to the addition of calcium rosinate (German—*Harzkalk*) which is frequently used in excessive quantities to give the dried coat of varnish a fictitious hardness and gloss, which disappear somewhat rapidly on exposure to moisture with formation of white spots, caused by the decomposition of the rosinate into rosin acid and lime.[1] The chemical examination must be supplemented by practical tests.

The practical examination of varnish for suitability and drying power is carried out in a similar fashion to that described above for boiled oils. The influence of the atmosphere (moisture, light, etc.) can only be observed by practically testing the varnishes themselves, or after mixing them with pigments.

A series of practical examinations of a number of boiled oils, varnish oils, and rosin oils, as regards drying power (by *Weger*) is given in Table No. 38 of the *Laboratory Companion to Fats and Oils Industries.*

Enamels.—Enamel paints (German—*Emaillefarben*) is a trade term given to mixtures of varnishes with pigments (such as zinc oxide, lead oxide, iron oxide, etc.). For their chemical examination the methods employed in the examination of both paints and varnishes must be combined.

IV. OXIDISED OILS

Under the term "oxidised oils" I comprise all those oils which have absorbed oxygen by exposure to the atmosphere, or have been oxidised artificially by heating ("blowing") in a current of air or oxygen gas.

From the explanation given in Chapter VII. (p. 305), it will be gathered that only the semi-drying oils and drying oils lend themselves to the manufacture of oxidised oils, although all oils and fats if blown with oxygen at an elevated temperature become oxidised with formation of volatile acids and "oxidised" acids. This has been shown by me to occur even in the case of "premier jus."[2] The behaviour of blubber oils and liquid waxes is similar to that of the semi-drying oils. Hence it is convenient to divide the oxidised oils into two classes, namely, those obtained from semi-drying vegetable oils, blubber oils, and liquid waxes, on the one hand, and those obtained from drying oils, on the other.

(1) Oxidised Oils from Semi-drying Vegetable Oils, Blubber Oils, and Liquid Waxes

These oxidised oils (termed commercially "blown oils," "base oils," "thickened oils," "soluble castor oils") are prepared by heating

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[1] Heupel, *Chem. Revue*, 1903, 125.

[2] *Analyst*, 1899, 322. Cp. Table 36 of *Laboratory Companion to Fats and Oils Industries.*

vegetable semi-drying oils, blubber oils, or liquid waxes in a current of air to a somewhat elevated temperature. The vegetable oils, blubber oils, or liquid waxes are placed in a jacketed pan or cylindrical vessel provided with a steam coil and stirring arrangement (somewhat similar to the apparatus shown in Fig. 69), so that the oil is agitated whilst the air is blown through it, the object of the agitation and spraying by the air current being to produce as complete a contact as possible of the oil with air. Whilst air is blown through the oils, steam is sent through the coil so as to bring the temperature up to 70° C. or more, in some cases even to 110-115° C. The agitation and blowing is continued until the desired specific gravity is reached. During the blowing some volatile fatty acids escape, as also some insoluble acids, which are carried away by the current of air. In some cases the temperature rises beyond that of the steam used for heating, so that it is frequently required to cool the "blown" oil by passing cold water through the jacket of the pan or the coil of the vessel, as the case may be. In consequence of this treatment the oils increase in density and in viscosity. They approach in these respects castor oil, but differ from it in that they are miscible with mineral oils; hence the commercial term "soluble castor oil" was given to them. They further differ from castor oil in their sparing solubility in alcohol. The most prominent chemical change the oils undergo through "blowing" may be gathered from the following tables in which I have collated a number of observations on oils which have been oxidised on a laboratory scale, and contrasted them with the original oils from which they have been prepared.

Oxidised Oils prepared in the Laboratory, see table facing this page.

OXIDISED OILS PREPARED IN THE LABORATORY

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.			XIII.	XIV=VIII−(IV+XIII.)			
Oil.	Specific Gravity at 15·5° C. (Water 15·5=1).	Free Acid Calculated as Oleic.	Unsaponifiable Matter.	Saponification Value.	Iodine Value.	Specific Temperature Reaction.	Insoluble Acids (Hehner Value).	Soluble Volatile Acids.	Soluble Non-Volatile Acids.	Iodine Value of Insoluble Acids.	Molecular Weight of			Oxidised Acids.	Non-Volatile Fatty Acids freed from Oxidised Acids and Unsaponifiable.			Observer.
											Insoluble Acids.	Soluble Non-Volatile Acids.	Soluble Volatile Acids.		Per cent.	Molecular Weight.	Melting Point °C.	
		Per cent.	Per cent.				Per cent.	Per cent.						Per cent.				
Rape	0·9141	5·10	0·65	173·9	100·5	135	94·76	0·52		...	...	...	...	...	...	...	...	Thomson and Ballantyne[1]
,, Blown 5 hours . .	0·9275	5·01	...	183·0	88·4	...	...	...	...	...	...	...	...	...	...	...	...	,,
,, Blown 20 hours . .	0·9615	7·09	0·76	194·9	63·2	...	85·94	9·20	0·82	66·5	327	241	72	...	...	...	...	,,
Sperm	0·8797	1·97	36·32	130·4	82·1	...	...	...	...	...	...	...	...	...	...	...	...	,,
,, Blown 25 hours . .	0·8989	3·27	34·65	142·3	67·1	...	...	...	...	...	...	...	...	...	...	...	...	,,
Cotton seed	...	1·1	1·05	190·4	108·8	...	94·22	...	...	...	...	...	...	0·27	92·9	278·1	35·36	Fahrion
Oxidised Cotton seed obtained by exposure on chamois leather (page 309) and exhausting with petroleum ether—																		
After 8 days . . .	...	6·69	1·13	223·1	55·4	...	85·34	...	...	...	...	...	...	20·62	63·59	276·2	45·46	,,
After 12 days . .	...	6·94	1·33	227·5	46·3	...	83·62	...	...	...	...	...	...	19·13	63·16	273·2	46	,,
Oil obtained by subsequent exhaustion with ether of the leather extracted with petroleum ether	...	16·79	0·72	271·3	29·1	...	74·20	...	...	...	...	...	...	37·72	35·76	269·1	51	,,

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[1] *Journ. Soc. Chem. Ind.* 1892, 506.

Oxidised Cotton Seed Oil (Lewkowitsch)

	Original Oil.				Acetylated Oil.				
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
	Specific Gravity at 15·5° C.	Saponification Value.	Total Volatile Fatty Acids per Gram in terms of Milligrams, KOH.	Oxidised Acids. Per cent.	Saponification Value.	Hehner Value.	Apparent Acetyl Value.	True Acetyl Value.	Difference, V. – II.
Cotton seed oil . .	0·9250		0·1		200·2	95·7	7·7	7·6	
Cotton seed oil, blown 2 hours at 120° C. .	0·9262	194·3	2·88	0·51	203·9	94·8	14·2	11·32	9·6
Cotton seed oil, blown 4 hours at 120° C. .	0·9291	194·9	2·44	0·87	212·0	92·9	22·9	20·46	17·1
Cotton seed oil, blown 6 hours at 120° C. .	0·9350	196·1	4·60	0·94	215·2	91·9	30·0	25·4	19·1
Cotton seed oil, blown 10 hours at 120° C. .	0·9346	196·8	4·16	1·28	218·4	91·4	35·0	30·84	21·6

In the table facing this page the results of the analysis of some commercial "blown" oils are recorded.

It will be noticed that a considerable amount of lower fatty acids has been formed, as is indicated by the high saponification value and the Reichert-Meissl value. The amount of oxidised acids formed having been determined in a few cases only, it seemed important to ascertain whether the oxidised acids form a characteristic constituent of the blown oils. With this object in view, the author has carried out an examination of several typical commercial blown oils, namely, blown ravison oil, blown East India rape oil, blown cotton seed oil, and blown maize oil. The results of the investigation are given in the four following tables (pp. 985, 986):[1]—

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[1] Cp. *Analyst*, 1902, 683.

[TABLE

Some Constants and Variables of Commercial Blown Oils

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.	XIII.	XIV.		XV.	XVI.	XVII.	XVIII.
No.	Oil.	Specific Gravity at 15·5° C. (water 15·5=1).	Free Acid calculated as Oleic.	Unsaponifiable Matter.	Saponification Value.	Reichert-Meissl Value.	Iodine Value.	Specific Temperature Reaction.[1]	Insoluble Acids (Hehner Value).	Soluble Volatile Acids.	Soluble Non-Volatile Acids.	Iodine Value of Insoluble Acids.	Molecular Weight of		Oxidised Acids.	Apparent Acetyl Value.	True Acetyl Value.	Observer.
													Insoluble Acids.	Soluble Volatile Acids.				
			Per cent.	Per cent.					Per cent.	Per cent.	Per cent.				Per cent.			
1	Blown rape . . .	0·9672	4·93	2·80	197·7	...	63·6	253	84·97	1·90	1·94	62·7	296·0	104	...	...	...	Thomson and Ballantyne[2]
2	,, ,, . .	0·9714	...	..	205·6	...	...	...	...	...	..	...	...	...	24·95	62·04	53·14	Lewkowitsch
3	,, ,, . . .	0·9772	8·5	..	163 (?)	...	47·2	...	...	...	...	...	...	...	...[3]	...	...	Lecocq and Dandervoort[4]
4	,, ,, . . .	0·9745	4·1	..	175·1	...	54·1	.	...	...	...	...	...	...	...[5]	.	.	
5	,, ,, . . .	0·9674	4·88	...	267·5	8·8	65·3	...	88·64	...	...	...	294·1	...	...	...	.	Gripper[6]
6	Blown Jamba . .	0·9169	...	0·65	174·9	...	99·5	...	95·90	...	...	...	311·0	...	0·53	...	...	Lewkowitsch
7	Blown cotton seed .	0·9740	3·38	1·00	213·2	...	56·4	227	...	...	...	...	...	...	...	...	...	Thomson and Ballantyne
8	,, ,, ,, .	At 20° C. (water 20°=1) 0·9722	..	...	213·7	...	...	...	...	...	...	...	...	...	26·45	65·6	48·54	Lewkowitsch
9	Blown seal . . .	0·9815	16·5	...	221·0	...	78·2	...	73·4	...	...	...	...	...	...	...	...	Chapman and Rolfe[7]

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[1] Cp. p. 317.

[2] *Journ. Soc. Chem. Ind.* 1892, 506.

[3] Iodine value of the oxidised fatty acids, 36 ; neutralisation value, 191.

[4] *Bull. de l'Assoc. Belge de Chim.* 1901, 325.

[5] Iodine value of the oxidised fatty acids, 29·7 ; neutralisation value, 189.

Journ. Soc. Chem. Ind. 1899, 342.

[7] *Chem. News*, 1894 (70) 2.

A. *Characteristics of "Blown" Oils (Lewkowitsch)*

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.	XIII.	XIV.
Blown Oil.	Neutralisation Value.	Saponification Value.	II. – I.	Iodine Value.	Total Soluble Acids.	Specific Gravity.	Un-saponifiable.	Oxidised Acids.	Hehner Value.	Acetyl Value. Apparent.	Acetyl Value. True.	Saponification Value of the Acetylated Oil.	Hehner Value after Acetylation.	XII. – II.
	Mgrms. KOH.	Mgrms. KOH.	Mgrms. KOH.	Per cent.	Mgrms. KOH.		Per cent.	Per cent.		Mgrms. KOH.	Mgrms. KOH.	Mgrms. KOH.		
Ravison rape .	10·47	198·31	187·84	72·66	35·89	0·9685	1·23	21·22	83·52	88·37	52·93	243·2	...	44·9
East India rape	13·25	215·57	202·32	61·92	56·26	0·9623	0·93	20·74	82·18	102·87	46·61	253·33	...	37·76
Cotton seed .	9·41	224·59	215·18	65·74	46·49	0·9785	1·37	29·39	82·59	110·73	64·29	273·30	83·85	48·71
Maize . .	7·33	208·63	201·30	90·7	49·13	0·9806	2·28	31·93	82·34	113·16	63·37	268·75	...	60·1

B. *Characteristics of the Mixed Fatty Acids (Lewkowitsch)*

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
Mixed Fatty Acids from	Neutralisation Value.	Saponification Value.	II. – I.	Iodine Value.	Total Soluble Acids.	Hehner Value.	Acetyl Value. Apparent.	Acetyl Value. True.	Saponification Value of Acetylated Acids.	IX. – II.	Hehner Value of the Acetylated Acids.
	Mgrms. KOH.	Mgrms. KOH.	Mgrms. KOH.	Per cent.	Mgrms. KOH.		Mgrms. KOH.	Mgrms. KOH.	Mgrms. KOH.		Per cent.
Blown ravison rape oil .	175·14	191·7	16·56	73·31	7·26	...	50·0	42·75	227·4	35·7	...
Blown East India rape oil	171·93	190·0	18·07	60·80	10·71	...	66·2	55·5	237·8	47·8	...
Blown cotton seed oil .	194·79	210·46	15·67	72·43	12·94	93·76	67·35	55·67	254·8	44·4	92·11
Blown maize oil . .	192·8	209·93	17·13	88·08	29·45	86·4	88·97	59·52	267·3	57·37	..

C. *Characteristics of Oxidised Acids (Lewkowitsch)*

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
Oxidised Acids from	Neutralisation Value.	Saponification Value.	II. – I.	Iodine Value.	Total Soluble Acids.	Hehner Value.	Acetyl Value.		Saponification Value of Acetylated Acids.	IX. – II.	Hehner Value of Acetylated Acids.
							Apparent.	True.			
	Mgrms. KOH.	Mgrms. KOH.	Mgrms. KOH.	Per cent.	Mgrms. KOH.		Mgrms. KOH.	Mgrms. KOH.	Mgrms. KOH.		
Blown ravison rape oil .	171·5	208·0	36·5	49·14	22·56	...	102·5	80·0	307·5	99·5	...
Blown East India rape oil	173·3	211·3	38·0	39·79	22·35	...	128·0	105·65	315·9	104·6	...
Blown cotton seed oil .	174·7	220·71	46·01	48·6	36·12	...	154·4	118·28	322·69	101·98	83·85
Blown maize oil . .	171·94	215·74	43·60	70·87	48·0	93·53	173·58	126·68	326·45	111·11	...

D. *Characteristics of Fatty Acids freed from Oxidised Acids (Lewkowitsch)*

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.
Fatty Acids freed from Oxidised Acids from	Neutralisation Value.	Saponification Value.	II. – I.	Iodine Value.	Total Soluble Acids.	Hehner Value.	Soluble Acids.	Acetyl Value.		Saponification Value of Acetylated Acids.	X. – II.	Hehner Value of Acetylated Acids.
								Apparent.	True.			
	Mgrms. KOH.	Mgrms. KOH.	Mgrms. KOH.	Per cent.	Mgrms. KOH.	Per cent.	Mgrms. KOH.	Mgrms. KOH.	Mgrms. KOH.	Mgrms. KOH.		
Blown ravison rape oil .	176·8	188·6	11·8	61·88	6·97	...	6·75	42·5	35·53	220·3	31·7	...
Blown East India rape oil	166·6	176·8	10·2	55·93	10·09	...	8·85	47·13	37·54	219·2	42·95	...
Blown cotton seed oil .	188·0	196·15	8·15	56·02	11·0	...	7·27	33·69	22·69	232·0	33·6	96·17
Blown maize oil . .	172·37	177·68	5·31	85·52	6·14	85·54	7·54	43·8	36·7	228·76	50·52	...

The characteristics of the *blown oils* themselves are recorded in Table A. On washing the acetylated oils with water, emulsions were formed, but the separation of the acetylated oil from the water caused no difficulty. The blown ravison oil gave the most persistent emulsion. The characteristics of the *mixed fatty acids* are given in Table B. The *oxidised acids* (Table C) were separated from the mixed fatty acids in the manner described, p. 368. The saponification values of the oxidised acids are considerably higher than their neutralisation values; this proves that lactonic substances are present. On separating the lactones from the fatty acids in the manner described, p. 339, the supposed lactones were obtained as thick, viscous liquids, soluble in alcohol.[1] The fatty acids recovered from the soap solution were again found to contain notable quantities of lactones, apparently formed on liberating the acids from their soap solution. The lactones were again separated off in the same manner, and the soap solutions decomposed with mineral acid, but the liberated fatty acids were again found to contain lactones. The comparatively high iodine values of the oxidised acids point to a considerable amount of unsaturated fatty acids. (Since the oxidised acids are practically insoluble in carbon tetrachloride, the determination of the iodine value was carried out in alcoholic solution. The error introduced thereby cannot have been a considerable one; for whilst the blank test with carbon tetrachloride required 50·6 c.c. of thiosulphate, the alcoholic solution took 50·00 c.c.) Contrary to expectation the oxidised acids contained also notable amounts of soluble fatty acids. The explanation which suggested itself, namely, that these soluble acids were formed by treatment of the oxidised acids with alcoholic potash, was not borne out by experiments, as the oxidised acids which had not been treated with alcoholic potash lost, on washing with water, considerable amounts of soluble fatty acids.

The characteristics of the *fatty acids freed from oxidised acids* by petroleum ether are detailed in Table D. Their acetyl values are still considerable. It has not been ascertained yet whether these are due to the presence of petroleum ether—soluble hydroxylated acids. Also these acids contain lactones (although their amount does not exceed 4 to 6 per cent), as well as small amounts of soluble acids.

These results show that the oxidised oils consist of a complicated mixture of acids. The nature of these acids is being investigated by the writer. Since the blown oils yield practically the full amount of glycerol, it would appear necessary to study in the first instance the influence of "blowing" on the individual unsaturated fatty acids—oleic, erucic, linolic. Hitherto oleic acid only has been examined, with the result tabulated above (p. 369).

The blown oils find technical application as lubricating oils in admixture with other oils. They are said to be useful for lubricating purposes on account of their high specific gravities and viscosities. Opinions differ, however, as to their suitability, objection being taken to them on account of their liability to "gum" and their low flash

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[1] Cp. *Analyst*, 1902, 144.

points. Nevertheless, the blown oils are extensively used in admixture with mineral oils and even with rosin oils.

The longer fatty oils are "blown," the lesser becomes their miscibility with petroleum hydrocarbons. Jenkins[1] pointed out that the blown oils are least soluble in American petroleum hydrocarbons, more soluble in shale hydrocarbons, and comparatively easily soluble in Russian petroleum hydrocarbons.

It may perhaps be possible to base a method of differentiating the various hydrocarbons on their behaviour with oxidised oils.

(2) Oxidised Oils from Drying Oils

If drying (vegetable) oils are exposed to the atmosphere or to a current of air (oxygen) at a somewhat elevated temperature, the formation of oxidised acids proceeds much more rapidly than in the case of semi-drying oils.

Extensive use of this property is made in the application of paints and varnishes, the vegetable oil—chiefly linseed oil[2]—finally drying to a solid mass, which forms a coherent coat on the surface of the object to which a paint or varnish has been applied.

The chemical change which takes place when a vegetable oil "dries" to a solid elastic skin is but very imperfectly understood. The change appears, however, to be the same, whether raw linseed oil be allowed to absorb oxygen from the atmosphere slowly, or whether the "drying" be accelerated by previously converting the oil into "boiled" oil, or if the raw linseed oil be treated in a current of oxygen at a somewhat elevated temperature, after having been intermixed with driers. *Mulder's* opinion that in the first stage the glyceridic constituent of the oil is oxidised and that the liberated fatty acids take up oxygen and are converted into the anhydride of "hydroxylinoleic" acid (*i.e.* the anhydride of hydroxylated linseed oil fatty acids), a neutral substance, insoluble in ether, termed by him "linoxyn," must be rejected as erroneous, for this view postulates that hydrolysis of the glycerides precedes oxidation. But it has been pointed out already that the solid skin is not formed when the mixed fatty acids are exposed to the atmosphere. Moreover, *Bauer* and *Hazura*[3] have shown that at least in the first stage of oxidation the glyceridic constituent of the linseed oil remains intact and that the oil is converted by exposure in thin layers into a substance similar in its properties to *Mulder's* "linoxyn," but still representing a glyceride. This substance was assumed by *Bauer* and *Hazura* to be hydroxylinolein (*i.e.* a mixture of hydroxylinolin and hydroxylinolenin).

Fahrion has shown that when boiled oils dry, some of the fatty acids are converted into a class of acids for which I have suggested

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[1] Cp. *Analyst*, 1902, 145.

[2] With regard to tung oil, cp. Kronstein, Engl. Pat. 1386, 1901.

[3] *Monatshefte f. Chem.* 9, 459; *Zeit. f. angew. Chem.* 1888, 455.

the name "oxidised" acids. These oxidised acids are formed to a very slight extent only during the process of boiling linseed oil. Therefore, in properly prepared boiled oils, no higher amount of oxidised acids is found than in polymerised linseed oil (lithographic varnish). On spreading three boiled oils (of the iodine values 101·3, 77·3, and 33·7, containing 0·5, 4·1, 7·6 per cent of oxidised acids respectively) in a thin film on a glass plate, and exposing the oils to the air for ten days at a somewhat higher temperature than the ordinary, *Fahrion* found that the proportions of oxidised acids had increased to 30·6, 20·8, and 16·4 per cent respectively.

It appears likely that in the first instance the linolenic acids are attacked, and that the linolic acid only plays a subordinate part, as otherwise maize and cotton seed oils would exhibit better drying powers than they actually possess.

With a view to investigating the changes which take place when linseed oil dries, I have treated linseed oil at 120° C. with a current of air for a varying number of hours, or, in other words, prepared "blown" linseed oils. The results obtained on examining the products are set out in the following table :—

[TABLE

Characteristics of Oxidised ("Blown") Linseed Oil (Lewkowitsch)

	Oxidised Oil.				Acetylated Oil.				
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
	Specific Gravity at 15·5° C.	Saponification Value.	Total Volatile Fatty Acids in terms of Milligrams, KOH.	Oxidised Acids. Per cent.	Saponification Value.	Hehner Value.	Apparent Acetyl Value.	True Acetyl Value.	Difference, V. – II.
Linseed oil	...	...	0·8	...	205·6	96·2	12·5	11·7	...
Linseed oil, blown 2 hours at 120° C.	0·9334	189·8	1·68	1·2	200·9	94·4	18·9	17·22	11·1
Linseed oil, blown 4 hours at 120° C.	0·9403	191·3	3·0	1·7	203·9	94·6	22·5	19·5	12·6
Linseed oil, blown 6 hours at 120° C.	0·9446	192·4	8·3	5·03	208·2	93·2	25·5	17·2	15·8
Linseed oil, blown 10 hours at 120° C.	0·9460	192·7	0·9	7·1	211·8	92·1	32·6	31·7	19·1

If the oxidation of linseed oil is carried further, *i.e.* until linseed oil has taken up the maximum amount of oxygen, a flexible solid mass is obtained, termed "solidified (linseed) oil," "solid linseed oil," "oxidised linseed oil" ("linoxyn").

Leeds examined two oxidised oils which had been obtained by treating linseed oil with oxygen in a jacketed pan. They are contrasted in the following table with a sample of completely dried oil obtained from a raw linseed oil exposed in a flat dish to a moderate current of air at 45° C. for about five weeks, the skin formed being daily broken up and mixed with the bulk. This dried linseed oil had a jelly-like consistence, lumps of comparatively hard material and skin alternating with a small quantity of oil of the consistence of "middle" varnish :—

Oxidised Linseed Oil prepared by Treatment with Oxygen

Oils.	Specific Gravity at 15° C.	Free Acid calculated as Oleic Acid.	Saponification Value. Mgrms. KOH.	Unsaponifiable Matter.	Oxidised Acids.	Iodine Value.
		Per cent.		Per cent.	Per cent.	
Oxidised oil, weak	1·03	18 - 28·4[1]	221	0·89	42·82	58·8
„ „ strong	1·05	18·49-28·9[1]	223·5	0·97	44·19	53·5
Dried linseed oil .	...	12·67	171·6	0·81	31·58	93·9

Mixed Fatty Acids.	Melting Point.	Solidifying Point.	Mean Combining Weight.	Saponification Value.	Iodine Value.
	°C.	°C.			
Oxidised oil, weak .	28	26	241·4	232·4	63·2
„ „ strong .	27	25	242·5	231·3	60·6
Dried linseed oil .	26	22	268·8	208·7	100·3

The fact that oxidised linseed oil has absorbed considerable amounts of oxygen is brought out by the following elementary analyses due to *Williams* :[2]—

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[1] The first of these figures was found when the pink colour of the phenolphthalein remained after a vigorous shaking ; but it disappeared after a short time, and more alkali was run in until the pink colour remained constant for two or three minutes ; thus the second figure was obtained (cp., however, *Journ. Soc. Chem. Ind.* 1890, 847).

[2] *Analyst*, 1898, 253.

[Table

	Carbon.	Hydrogen.	Oxygen.
	Per cent.	Per cent.	Per cent.
Solid oil I.	74·32	10·04	15·64
,, II.	69·74	9·57	20·69
,, III.	69·52	9·49	20·99
,, IV.	64·74	9·01	26·25
,, V.	65·40	9·00	25·60
,, VI.	68·64	9·24	22·12
,, VII.	64·38	9·01	26·61
Raw oil	75·03	10·78	14·19
,,	75·40	10·64	13·96

The solid oil is notable for its high amount of oxidised acids. A few characteristics of the oxidised acids prepared from solidified linseed oil have been given above (p. 369). Recently I have more fully examined[1] a solidified oil. In the following table I collate the results obtained hitherto :—

Characteristics of Solid Linseed Oil (Linoleum Mass) and its Acids (Lewkowitsch)

		Solid Oil.	Total Fatty Acids.	Oxidised Acids.	Fatty Acids freed from Oxidised Acids.
I.	Neutralisation value	...	209·63	...	179·97
II.	Saponification value	287·47	248·74	...	187·58
III.	II. – I.	...	39·11	...	7·61
IV.	Iodine value	52·2	60·27	46·49	61·31
V.	Total soluble acids	136·9	59·57	59·68	18·89
VI.	Unsaponifiable	1·33	...	...	...
VII.	Oxidised acids	53·01 per cent	...	...	...
VIII.	Hehner value	53·92	81·32	...	...
IX.	Apparent acetyl value	...	115·01	164·67	50·25
X.	True acetyl value	...	55·04	104·99	31·36
XI.	Saponification value of the acetylated product	367·75	304·24	341·43	246·11
XII.	Hehner value of the acetylated product	...	84·4	76·38	96·05
XIII.	XI. – II.	...	55·5	86·29	58·53

Further investigation is required to elucidate the changes which linseed oil undergoes whilst it is converted into solid oil.

Solidified oil is heavier than water and practically insoluble in ether, chloroform, and carbon bisulphide. On a large scale this substance is prepared by two methods. The first consists in allowing linseed oil, previously "boiled" with a drier in order to accelerate the oxygen

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[1] Lewkowitsch, *Analyst*, 1902. 140.

absorption, to run over "scrim," a light cotton fabric, hanging down from the ceiling of a high building, the temperature of which is kept at about 100° F. A portion of oil solidifies on the fabric; the oil which drains off is again pumped up and allowed to run down until the layers of the solid mass have reached (after several weeks) the thickness of about half an inch. This process is termed the "scrim process"; the solidified oil obtained by this method is termed "scrim oil."

The second method consists in passing a current of oxygen gas through linseed oil intermixed with a drier and heated by steam in jacketed pans. When the maximum amount of oxygen has been absorbed, the mass forms a thick viscous fluid, which will still run whilst hot, but solidifies on cooling to a substance similar to the "scrim oil." During the "blowing" a certain decomposition and oxidation of the glycerol formed takes place, as notable quantities of acroleïn vapours escape. The solid oil so obtained has not the same elastic properties which the "scrim oil" possesses, no doubt due to the fact that in the scrim oil the destruction of glycerol is much smaller, and the oxidation does not proceed as far as to the formation of "superoxidised oil" (see below). Whether these two kinds of solid oil are identical in their composition, and furthermore, whether they are identical with the elastic skin obtained when "boiled oil" dries, has not yet been ascertained.

The solid linseed oil is used on an extensive scale in the manufacture of **linoleum**,[1] the solidified oil being mixed with various gum-resins, rasped cork, and "fillers." The mass so obtained is termed linoleum cement. It is rolled on to a jute canvas-backing, and is finally "seasoned" at a temperature of 75° F. before being placed on the market in its well-known form.

The valuation of linoleum is almost exclusively based on "practical" tests. Still, an excessive amount of ash will be revealed by chemical analysis, and on treating the comminuted mass with ether the extract will show whether the oil had been treated with a sufficient amount of oxygen. The methods employed for testing linoleum at the *Königliche Technische Versuchs-Anstalten*[2] embrace determinations of specific gravity, weight per square centimetre, thickness, resistance to wear, bending tests over mandrils of 10 to 45 mm. diameter, tensile strength, extensibility, permeability to water and the action of weak acids, alkalis, and petroleum.

The solid linseed oil ("linoxyn") was up to recently looked upon as being the ultimate product of oxidation.

Reid,[3] however, has shown that the solid oil is still liable to further oxidation, he having obtained from it a viscous liquid, heavier than water, and soluble in it to a considerable extent. This liquid is termed by *Reid* "super-oxidised" linseed oil. The decay

[1] Cp. W. F. Reid, *Journ. Soc. Chem. Ind.* 1896, 75.

[2] Burchartz, *Mitth. Königl. Techn. Vers.-Anst.* 1899, 285.

[3] *Journ. Soc. Chem. Ind.* 1894, 1020.

which paints and varnishes exposed to the atmosphere undergo in course of time may be explained by the formation of this super-oxidised oil, which is washed away by rain water. Linoleum undergoes this change at a much slower rate.

V. VULCANISED OILS, RUBBER SUBSTITUTES

French—*Gomme factice.* German—*Kautschuksurrogate, Faktis.*

The action of sulphur chloride on oils and fats has been described in Chapter VII. p. 302; it has been also pointed out (p. 322) that a considerable amount of heat is evolved when sulphur chloride interacts with oils and fats.

The action of sulphur on oils and fats is much slower. At the ordinary temperature no chemical change takes place; at elevated temperatures, however, sulphur does react with the oils and fats in a manner that may be likened to the absorption of oxygen at the ordinary temperature. The products obtained by the reactions are solid bodies which possess some degree of elasticity, and are therefore used as rubber substitutes.

The manufacture of these substitutes is carried out in a similar manner to the vulcanising of india-rubber, namely, either by treating oils with sulphur at a somewhat elevated temperature, comparable to the "hot cure" of vulcanising india-rubber, or by treatment with sulphur chloride in the cold, corresponding to the "cold cure" in the vulcanising of india-rubber. Hence the term "vulcanised oils" is appropriately applied to these products.

According to the process used the vulcanised oils are differentiated in the trade as "brown" (black) and "white substitutes" respectively. The "white substitutes" contain, therefore, a considerable proportion of chlorine, which is, of course, absent in the "brown (black) substitutes"; thus it is possible to easily distinguish by chemical means the two classes of rubber substitutes.

The white substitutes form a yellowish, elastic, crumbly substance of oily smell and neutral reaction; the brown (black) substitutes occur in commerce either as sticky lumps or as a coarsely ground powder.

To manufacture the white substitutes a suitable oil, especially rape oil, castor oil, and also arachis oil,[1] is dissolved in carbon tetrachloride, in a wooden, or earthenware, or enamelled iron vessel. Whilst the oil is agitated, sulphur chloride is run in,[2] the agitation being continued until the mass has solidified. The reaction is accompanied by evolution of hydrochloric acid gas.

The brown substitutes are manufactured by heating oil with sulphur to 160° C.

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[1] Linseed oil and cotton seed oil are less suitable.

[2] Höhn (*Chem. Rev.* 1900, 113) states that in the case of colza oil not less than 17 per cent of sulphur chloride must be used.

The nature of the chemical change which takes place is not yet fully understood, and little can be added to the notes given above (chap. vii. p. 303), under the head of sulphur chloride. *Henriques* has shown that blown oils require much less sulphur chloride than the original oils to form vulcanised oils; this seems to favour the opinion that the white substitutes are addition products. On saponification, the chlorine only is eliminated as hydrochloric acid, the sulphur remaining in chemical union with the oils, so that unsaturated substances are again obtained, as is proved by the high iodine numbers of the sulphurised fatty compounds. The sulphur cannot be present as an SH group, as the acetyl values of the substitutes are low.

Nor is the reaction of sulphur on oils fully understood. Whereas melted sulphur does not interact with a saturated fatty acid, such as stearic acid, at about 130° C., oleic acid[1] readily absorbs ten per cent of sulphur at 130°-150° C. The sulphur does not crystallise out on cooling, and no sulphuretted hydrogen is evolved. The reaction which takes place appears therefore to consist in true addition. It differs most essentially from the action of sulphur on oils at higher temperatures, for even stearic acid is attacked by sulphur at 200° C. with evolution of sulphuretted hydrogen, much as oleic acid heated with sulphur to 200°-300° C. is converted into sulpho-oleic acid with concomitant formation of sulphuretted hydrogen (cp. chap. iii. p. 105).

Altschul states that all oils behave in the same manner, viz. form with sulphur addition compounds, which on saponification yield salts of sulphurised fatty acids; the latter are obtained in their free state on decomposing with a mineral acid.

Henriques[2] has, however, shown that the reaction is not so simple, addition and substitution taking place concurrently, the former preponderating at lower temperatures, the latter at high ones. Also *Michael*[3] has shown that the action of sulphur on unsaturated organic compounds is of a complicated nature.

For the examination of the india-rubber substitutes the quantitative reactions naturally lend themselves as suitable methods, supplemented, of course, by such tests as the nature of the substance requires.[4]

It should be noted that the saponification of the sulphurised oil must be carried out in the cold in order to avoid loss of sulphur. In this case *Henriques'* method of cold saponification described above (chap. ii. p. 58) will be found suitable.

The content of sulphur is estimated by treating the substitute with fuming nitric acid in the presence of silver nitrate, and subsequently fusing with caustic potash and potassium nitrate. The insoluble silver compounds contain all the chlorine.

The following table reproduces some analyses of india-rubber substitutes by *Henriques*:[4]—

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[1] Altschul, *Journ. Soc. Chem. Ind.* 1896, 282.

[2] *Journ. Soc. Chem. Ind.* 1896, 282.

[3] *Berichte*, 1895, 1633.

[4] *Journ. Soc. Chem. Ind.* 1894, 47, 70.

Oils vulcanised with S_2Cl_2.	Sulphur.	Chlorine.	Water.	Residue on Ignition.	Fatty Acids.	Iodine Value.	Acetyl Value.	Fatty Acids.		
								Sulphur.	Chlorine.	Iodine Value.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.		Per cent.	Per cent.	
Linseed oil rubber substitute from raw oil . .	9·34	8·84	3·02	...	79·6	56·3	21·0	9·88	Trace	160·3
Linseed oil ,, ,, ,, blown oil .	4·78	4·85	0·85	...	81·67	52·6	19·6	4·06	0·60	141·2 121·0
Rape oil ,, ,, ,, commercial oil .	8·28	7·62	...	...	86·89	32·5	31·0	8·34	Trace	101·5
Rape oil ,, ,, ,, blown oil . .	6·59	5·95	...	...	87·95	26·9	...	6·54	Trace	102·8
Poppy seed oil ,, ,, ,, blown oil . .	7·68	7·44	...	...	74·90	33·6	...	8·32	...	133·3
Cotton seed oil ,, ,, ,, blown oil . .	6·23	5·36	...	...	...	30·3	51·3	6·44	Trace	91·5
Castor oil ,, with minimum of S_2Cl_2 .	4·82	6·70	...	...	85·35	35·2	...	5·32	Trace	136·2 147·4 152·1
Castor oil ,, ,, maximum ,, ,, . .	10·60	8·95	...	...	...	21·9	105·6	...	0·26	105·6
Commercial Products.										
White substitute, No. 1	6·4	5·0	0·85	0·8	90·45	30·9	...	6·12	0·83	91·3
,, ,, No. 2	6·17	5·86	1·0	5·51	73·58	31·0	...	6·45	0·43	91·2
,, ,, No. 3	8·25	8·88	...	...	...	32·6	...	8·15	...	102·3
Brown substitute, No. 1	15·48	0·7	...	...	...	42·0	...	14·14	...	129·0
,, ,, No. 2	17·71	0·36	...	...	...	42·0	...	15·20	...	125·6

Tung oil[1] and also fish oils have been subjected on a large scale to the same treatment, but hitherto the products so obtained have not found practical application. The body prepared by saturating fibrous material with fish oils and subjecting the mass to treatment with sulphur chloride was known under the fancy name "volenite."[2]

Recently the application of india-rubber substitutes to the manufacture of dynamite as an absorbent in the place of kieselguhr has been patented.[3]

VI. NITRATED OILS

On treating linseed oil or castor oil with a nitrating mixture, such as is employed in the manufacture of nitroglycerin—two parts (by weight) of concentrated sulphuric acid, 1·845, and one part of nitric acid, specific gravity 1·5—"nitrated" oils are obtained.[4] The nitrated oils are heavy, viscid liquids, heavier than water; thus the product obtained from linseed oil has the specific gravity 1·112, that from castor oil 1·127. The nitrated castor oil is insoluble in carbon bisulphide. The composition of these substances is not yet known. They contain 4 to 5 per cent of nitrogen. Samples examined by the author had high saponification values, varying from 278·5 to 286·5.

The most prominent property of these products is that of forming homogeneous compounds with nitro-cellulose. Thus a mixture of one part of nitrated castor oil with nine parts of nitro-cellulose yields a product resembling ebonite.

Solutions of these compounds in acetone are used as varnish, basis for paint, and for enamelling leather.

VII. SULPHONATED OILS, TURKEY-RED OILS[5]

The action of concentrated sulphuric acid on oils and fats has been explained already (p. 28). This reaction is employed on a large scale in the manufacture of Turkey-red oils.

Turkey-red oil is a fatty substance used in the preparation of the cotton fibre for dyeing and printing Turkey-red. The part which the

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[1] A salve-like substance obtained by heating tung oil with 0·5-10 per cent of sulphur until a clear solution results has been patented by Alexander, German Patent, 137340.

[2] Cp. also Scammell and Muskett, English Patent, 21229, 1901; French Patent, 319074; and United States Patent, 724618.

[3] German Patent, 110621.

[4] W. F. Reid, *Journ. Soc. Chem. Ind.* 1899, 972. Reid and Earle, English Patent, 21995, 1895; Velvril Company, German Patent, 103726.

[5] Frémy, *Ann. de Phys. et de Chim.* 65. 121; *Annalen*, 19. 296; 20. 50. Müller-Jacobs, *Journ. Soc. Chem. Ind.* 1884, 257; 412. 1885, 18; 21; 115. Liechti and Suida, *Journ. Soc. Chem. Ind.* 1886, 662. H. Schmid, *Dingl. Polyt. Journ.* 254. 346. Sabanejeff, *Berichte*, 19, Ref. 239. M. and A. Saytzeff, *Berichte*, 19, Ref. 541. Benedikt and Ulzer, *Journ. Soc. Chem. Ind.* 1887, 543; 1888, 328. Geitel, *Journ. prakt. Chemie*, 1888, 53. Löchtin, *Journ. Soc. Chem. Ind.* 1890, 498. Scheurer-Kestner, *Journ. Soc. Chem. Ind.* 1891, 471, 555. Wilson, *Journ. Soc. Chem. Ind.* 1891, 26; 1892, 495. Juillard, *Journ. Soc. Chem. Ind.* 1892 355; 1893, 528; 1894, 820. Wolff, *Chem. Revue*, 1897, 103. v. Niederhausen, *Bull. Soc. Ind.*, Mulhouse, 72, 389.

Turkey-red oil plays is not fully understood yet. Opinions differ as to whether the Turkey-red oil exercises a physical or a chemical action. The advocates of the former explanation assume that the oil protects the lake formed on the fibre, much as boiled linseed oil serves to protect a painted surface. The supporters of the chemical theory hold that the Turkey-red oil combines with alumina and finally with the colouring matter to form a compound lake. In those cases, however, where chemical combination with formation of a lake is excluded on account of the chemical constitution of the colouring matter, the physical theory appears to commend itself. Thus the Turkey-red oil is not a mordant proper, but acts as a fixing agent in so far as it imparts to the dyed fabric a better and superior lustre, which does not belong to the unoiled fibre.

Before the process of sulphonating castor oil was discovered, rancid olive oil (see p. 631) was used as a Turkey-red oil. At present Turkey-red oil is prepared by allowing concentrated sulphuric acid to run into *castor oil* slowly with constant stirring, taking care that the temperature of 35° C. is not exceeded. If necessary, the mass must be cooled, as at temperatures above 35° C. secondary reactions take place with liberation of sulphurous acid. The product is then mixed with water and allowed to settle out. The lower layer is drawn off and washed with a solution of Glauber's salt, until the washings are only slightly acid. Finally ammonia is added, until a sample gives a complete emulsion with a small quantity of water. Instead of ammonia some manufacturers use soda, or a mixture of ammonia and soda. Since the sulphonated oil is not completely neutralised by alkali, the resulting product still possesses a strong acid reaction.

The sulphonated oil, as obtained by the treatment with concentrated sulphuric acid, can be resolved into two portions by dissolving it in ether, washing with brine until it is free from sulphuric acid, and then shaking out repeatedly with water. On treating the united aqueous solutions with sodium chloride the *water-soluble portion* separates as an oily layer. On evaporating off the ether from the ethereal solution the *water-insoluble portion* is obtained.

Benedikt and *Ulzer* have shown that the *water-soluble portion*, in the case of a Turkey-red oil prepared from castor oil, consists of *ricinoleo-sulphuric acid* (see p. 118).

This acid is miscible with water in all proportions; the aqueous solutions lather like ordinary soap solutions. From these solutions the ricinoleo-sulphuric acid is precipitated as a heavy oily layer by brine, moderately dilute sulphuric acid, or hydrochloric acid.

By adding salts of calcium, barium, lead, copper, etc., to the solution of the acid, viscous precipitates are obtained. On boiling the aqueous or alkaline solutions of ricinoleo-sulphuric acid the acidic portion remains intact. If, however, the free acid be boiled with dilute hydrochloric or sulphuric acid it is readily decomposed into ricinoleic and sulphuric acids.

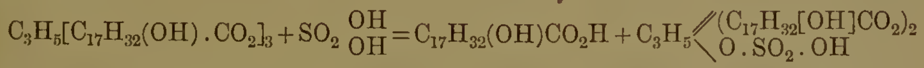
The *water-insoluble* portion of castor turkey-red oil consists chiefly of free ricinoleic acid and small quantities of neutral (unacted on) oil, and very likely also of anhydrides of ricinoleic acid (cp., however, *Bogajewsky*, below).

Scheurer-Kestner is of the opinion that castor turkey-red oil consists of ricinoleo-sulphuric acid, and monoricinoleic and diricinoleic acids, due to polymerisation of free ricinoleic acid.

According to *Juillard*, polymerisation proceeds further, giving rise to the formation of di-, tri-, tetra-, and penta-ricinoleic acids, an opinion at variance with *Scheurer-Kestner's* views, who maintains that polymerisation extending beyond the formation of the di-acid is due to a secondary action of hydrochloric acid, liberated on washing the product with brine instead of Glauber's salt. In *Juillard's* opinion castor turkey-red oil is a mixture of varying proportions of polyricinoleic acids of alkali salts of mono- and poly-ricinoleo-sulphuric acids, of anhydrides of the latter acids, and of their products of decomposition[1] (cp. also p. 118).

Bogajewsky[2] is of the opinion that the action of concentrated sulphuric acid ($\frac{1}{2}$ to 3 parts of SO_4H_2) on castor oil takes place in the following three stages:—

(1) Free ricinoleic acid is formed according to the following equation:—



$$C_3H_5[C_{17}H_{32}(OH).CO_2]_3 + SO_2\begin{matrix}OH\\OH\end{matrix} = C_{17}H_{32}(OH)CO_2H + C_3H_5\begin{matrix}\diagup\!\!\!\diagup(C_{17}H_{32}[OH]CO_2)_2\\ \diagdown O.SO_2.OH\end{matrix}$$

and the products of the interaction are completely saponifiable by half-normal alcoholic potash.

(2) The products formed in the second stage can no longer be completely saponified by means of half-normal alcoholic potash; the acid number of the product is decreased, the sulpho-groups exchanging places with the hydrogen of the hydroxyl-groups, thus—

$$(C_{17}H_{32}[OH]CO_2)_2C_3H_5(O.SO_2.OH) + SO_4H_2 =$$
$$(C_{17}H_{32}.[OSO_2OH]CO_2)_2C_3H_5.OH + H_2O.$$

In the aqueous solution partial dissociation takes place on standing; in alcoholic solution partial esterification occurs, dissociation in the one case and esterification in the other increasing as the proportion of sulphuric acid and the temperature rise.

(3) In the third stage the acid value decreases whilst the saponification value increases, the poly-ricinoleic compounds, described by *Juillard*, being formed.

On treating the product obtained in the second phase with 30 to 50 parts of water, the acid value increases to a maximum and then falls again; the maximum occurs when two hydroxyl groups have become free. On boiling, the triglyceride is almost completely decomposed with formation of ricinoleic and sulphuric acids.

In the manufacture of the normal commercial turkey-red oil the interaction of acid and oil is interrupted before the second stage has reached completion. The commercial product contains, therefore,

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[1] *Journ. Soc. Chem. Ind.* 1894, 820.

[2] *Chem. Centralblatt*, 1897, ii. 335.

chiefly the following substances:—(*a*) in the *water soluble* portion, ammonia (or soda) salts of the acids $(HO . SO_2 . OC_{17}H_{32} . CO_2)(HO . C_{17}H_{32} . CO_2) . C_3H_5 . (OH)$, and $HO . C_{17}H_{32} . CO_2H$; (*b*) in the *ether soluble* portion, unchanged castor oil and salts of the mixed castor oil fatty acids.

Besides castor oil also other fatty oils (such as olive oil, arachis oil, cotton seed oil, etc.) have been used for the production of turkey-red oils.

Benedikt expressed the view that castor turkey-red oil cannot be replaced by the oils named, because by treatment with sulphuric acid saturated hydroxylated acids and their sulphuric esters are formed, whereas castor turkey-red oil still consists of *unsaturated* fatty acids. *Benedikt*, therefore, ascribed the superior effect of castor oil to the oxidisability of the castor turkey-red oil fatty acids.

This statement, however, has not been supported by experiments. Its correctness is doubtful in view of the fact that the castor oil fatty acids are not readily oxidised by blowing (*Lewkowitsch*, p. 643). Besides, *Schmitz* and *Tönges*[1] have prepared a turkey-red oil by mixing oleic acid with sulphuric acid and heating the product to 105°-120° C. According to statements of *Werner*[2] this oil is, in certain cases, superior to castor turkey-red oil.[3]

The chemistry of turkey-red oils still requires further elucidation by experiments. Evidently similar reactions take place, as is the case in the acid saponification process (cp. chap. ii. p. 43; cp. also p. 1021). It may be added that *Geitel* (p. 105) has proved the presence of stearolactone and of the anhydride of the ordinary hydroxystearic acid in turkey-red oil prepared from oleic acid.

The commercial turkey-red oils are viscous, transparent fluids.

Since the chemical composition of a turkey-red oil depends on the mode of manufacture, the amount of sulphuric acid employed, and on the raw material used, the commercial products vary in their composition.

The commercial examination of a turkey-red oil divides itself into two parts, viz. (1) the practical examination, and (2) the chemical examination.

(1) *Practical Examination.*—The sample should give a complete emulsion with ten volumes of water. In practice the test is performed by mixing, in a graduated cylinder, one measure of oil, at first with a little warm water (with which the oil forms a clear solution). Then gradually increase the quantity until ten measures have been added and compare the appearance of the sample with an emulsion prepared side by side in exactly the same manner with a sample of known purity. No oily drops should separate after standing for a short time. An adulterated product may be recognised at

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[1] *Journ. Soc. Chem. Ind.* 1892, 827, German Patents 60579 and 64073.

[2] *Ibid.* 1893, 40.

[3] Cp. also Herbig, *Färber Zeitung*, 1902, 277; 1904, 24, 38.

this stage by not giving a clear solution with a small quantity of hot water, and also by a darker colouration than that observed in the case of a pure oil. The emulsions should show a slightly acid reaction to litmus paper. In case the emulsion be neutral or alkaline, acetic acid is added, drop by drop, until both samples show approximately the same acidity.

The most important test consists in dyeing cotton prepared with the oil. The sample dyeing is carried out in the following manner:—Two pieces of cotton of equal size are treated with the sample and with a standard oil respectively by allowing them to soak in an emulsion made from 1 part of oil and 15-20 parts of water. After drying, the fabric is mordanted with alum and dyed in alizarin, or steam red is printed on. The samples are then brightened by soaping and finished in the usual manner. The practical test will only be resorted to by a works' chemist, or by an analyst who has special experience in that branch of work.

(2) *Chemical Examination.*—A turkey-red oil is valued on the amount of **total fatty matter** in the sample. This comprises the *water-insoluble portion* obtained on adding a mineral acid to the oil (whereby fatty acids, hydroxy acids, and neutral oil are separated), as also the hydroxylated acids obtained on decomposing the soluble sulphuric esters of the fatty acids.

The **total fatty matter** may be determined by *Benedikt's* method.[1] About 4 grms. of the sample are weighed off accurately in a porcelain basin, and 20 c.c. of hot water are added gradually; should the liquid be turbid, ammonia is run in until the solution is slightly alkaline to phenolphthalein. A clear solution will thus be obtained. 15 c.c. of a sulphuric acid, prepared from equal measures of concentrated sulphuric acid and water, are next run in, and an accurately weighed quantity of paraffin wax, about 10 grms., are added. The mixture is heated until a clear fatty layer has separated on the top. After cooling the solidified cake is treated in the same manner as described under "Soap Analysis" and weighed.

The following rapid process, due to *Finsler*, and recommended by *Breindl*,[2] is largely employed in continental practice:—30 grms. of the sample are weighed off accurately, rinsed with about 70 c.c. of hot water into a flask of about 200 c.c. capacity, the neck of which is graduated in $\frac{1}{5}$ or $\frac{1}{10}$ c.c., 25 c.c. of sulphuric acid of specific gravity 1·563 (52° Bé.) are added, and the mixture is heated to boiling with frequent shaking until the fatty matter forms a clear, transparent layer. A hot concentrated solution of common salt, or Glauber's salt, is next added carefully to bring the separated layer of fat into the neck of the flask. After half an hour's standing the volume of fatty matter is read off; the number of c.c. multiplied by 3·33 corresponds to the total fatty matter expressed in per cents. Since, however, the specific gravity of the fatty matter is below 1, usually 0·945, a correction should be made.

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[1] *Zeitsch. f. angew. Chem.* 1887, 325.
[2] *Journ. Soc. Chem. Ind.* 1889, 573.

The total fatty matter thus found is less than the sulphonated oil dissolved in water by the amount of sulphuric acid split off on boiling with hydrochloric acid.

In addition to the total fatty matters the amount of (*a*) **neutral oil**, (*b*) **sulphonated fatty acids**, (*c*) **ammonia** or **soda**, and (*d*) **sulphuric acid** may be estimated.

(*a*) **Neutral Fat.**—30 grms. of the sample are dissolved in 50 c.c. of water; 20 c.c. of ammonia and 30 c.c. of glycerin are added, and the mixture exhausted twice with ether, using 100 c.c. for each extraction. The ethereal solution is then washed with water to remove small quantities of dissolved soap, and the ether is evaporated off. The residue is transferred to a small tared beaker, dried at first on the water-bath, then at 100° C., and weighed.

(*b*) **Sulphonated Fatty Acids.**—4 grms. of the sample are boiled in an Erlenmeyer flask with 30 c.c. of dilute hydrochloric acid (1 : 5) during 40 minutes, with frequent shaking. After cooling the liquid is transferred to a separating funnel, and shaken out with ether to extract the fatty matter. The aqueous layer is drawn off and the ethereal layer washed with water. The washings are united with the main aqueous portion, and the sulphuric acid determined by precipitation with barium chloride. From the amount thus found the quantity of sulphuric acid, as determined under (*d*) (see below), is subtracted and the difference calculated to ricinoleic acid, 80 parts of SO_3 corresponding to 378 parts of ricinoleo-sulphuric acid, $C_{18}H_{33}O_2 . O . SO_3H$.

(*c*) **Ammonia or Caustic Soda.**—7 to 10 grms. of the sample are dissolved in a little ether, and shaken four times with dilute sulphuric acid (1 : 6), using 5 c.c. each time.

To determine ammonia, the acid liquid is distilled with caustic potash in the well-known manner, and the ammonia received in an accurately measured quantity of standard acid.

To estimate caustic soda the acid liquid is concentrated in a platinum dish on the water-bath, and the excess of sulphuric acid driven off by heating on the sand-bath; the residue is mixed with ammonium sulphate, ignited, and the sodium sulphate weighed.

(*d*) **Sulphuric Acid.**—The quantity of sulphuric acid present in the form of ammonium or sodium sulphate is found by dissolving a weighed quantity of the sample in ether and shaking it several times with a few c.c. of concentrated brine free from sulphate. The several washings are united, diluted, filtered, and the filtrate precipitated with barium chloride.

The method for the detection of **iron** in turkey-red oils has been described p. 154.

If it be desired to determine the nature of the oils used in the manufacture of a sample of turkey-red oil, the acetyl value of the total fatty matter should be ascertained.

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[1] Herbig, *Chem. Revue*, 1902, 5.

An acetyl value of 125 or above will point to pure castor oil; in case other oils have been used, lower values will be obtained.

A sample of genuine castor oil examined in the writer's laboratory gave the following result:—

	Per cent.
Total fatty matter	40·1
Unsaponifiable	0·15

The examination of the fatty matter obtained by saponification led to the following numbers:—

	Per cent.
Specific gravity at 15° C.	0·9449
Iodine value	82·1
Acid value	174·3
Saponification value	189·3
Acetyl value	126·9

It may be mentioned here that *Scheurer*[1] proposed metallic sulpholeates—sulpholeate of aluminium—as mordants for steam colours. Sulpholeates of sodium, as also "oxyoleates" (freed from sulphonates, cp. p. 105), are frequently met with in commerce.

C.—INDUSTRIES BASED ON THE SAPONIFICATION OF OILS AND FATS

The important industries which are based on the hydrolysis (saponification) of oils and fats comprise the manufacture of stearine candles, soaps, and glycerin. The scientific principles which underlie the manufacture of these products have been fully discussed in Chapter II. from a theoretical point of view. In this section the industries founded on them will be considered from a practical point of view. Whereas the soap industry, like many of the older chemical industries, had reached a high degree of development on exclusively empirical lines, long before its scientific foundation was understood, the manufacture of stearine candles and of glycerin are the direct outcome of the scientific researches of *Chevreul*.

I. CANDLE INDUSTRY

In this work the chief attention must be paid to the manufacture of stearine candles; other materials used in the candle industry, such as beeswax, spermaceti, carnaüba wax, and the mineral waxes, can therefore only be considered briefly.

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[1] *Journ. Soc. Chem. Ind.* 1893, 1025.

1. STEARINE CANDLES, COMMERCIAL "STEARINE," COMMERCIAL STEARIC ACID

The saponification processes at present employed on a manufacturing scale in the stearine candle industry are the following:—

(1) Aqueous Saponification.
(2) Saponification with the Assistance of Bases.
(3) Sulphuric Acid Saponification. Acid Saponification.
(4) The Mixed Process.
(5) Saponification by means of Twitchell's Reagent.

(1) Aqueous Saponification

The realisation of the fundamental equation of fat hydrolysis:—

$$C_3H_5(OR)_3 + 3H.OH = C_3H_5(OH)_3 + 3R.OH$$

suggests itself to the candle maker as the ideal process. The first attempt to work such a process on an industrial scale was made by *R. A. Tilghmann*,[1] whose method consisted in forcing an emulsion of fat and water through a coiled iron tube heated in a furnace to a temperature of about 330° C. This process was, however, soon abandoned on account of the incomplete saponification and of the destruction of the fatty matter which took place. The efforts of later inventors to carry out the hydrolysis of fats in an autoclave by means of water have met with greater success. From the table "Aqueous Saponification of Neutral Fats under Pressure," p. 38, it will be gathered that with the increase of pressure under which the water acts on the glycerides, or in other words, with the increase of temperature of the heating steam, the rate at which hydrolysis takes place is much increased. In practice, steam at a pressure of 15 atmospheres = about 220 lbs. per square inch (corresponding to a temperature of about 200° C.), is capable of effecting hydrolysis to a very high extent.

The apparatus working on a practical scale in shown in Figs. 70, 71.

Fig. 70 represents *Hughes'*[2] apparatus, which the writer saw in operation in a Paris factory. The fat is charged into the autoclave A, about 30 per cent of water are added, and steam generated in a multitubular boiler at a pressure sufficiently high to keep up a working pressure of 15 atmospheres in the apparatus, is sent into the autoclave. The steam is finely divided into streamlets by a distributor similar to the one shown in Fig. 72. In order to provide additional security against explosion beyond that afforded by the safety valve, and in order to thoroughly agitate the mass, a small

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[1] English Patent, 47, 1854.

[2] English Patent, 6562, 1885.

amount of steam is allowed to escape continuously through the pipe E, which thus serves as an extra safety valve. The escaping steam is made use of for the concentration of a glycerin solution charged (through pipe G) into vessel B, in which is enclosed a heating coil connected with E, the condensed water escaping through valve F, which latter acts as a kind of steam trap. The steam evolved from the glycerin solution in B serves to pre-heat a dilute glycerin solution fed into vessel C at J. In consequence of the high temperature the fatty material becomes seriously discoloured, so that the fatty acids must be chiefly worked up by the "mixed process" (No. (4)). Moreover, since the hydrolysis of the fat does not reach so high a percentage as is the case in the processes described under 2, a small percentage of lime, about 1 per cent, is usually added to the mass in the autoclave. Hence, practically speaking, this method approaches very nearly those applied in the lime saponification process (p. 1007).

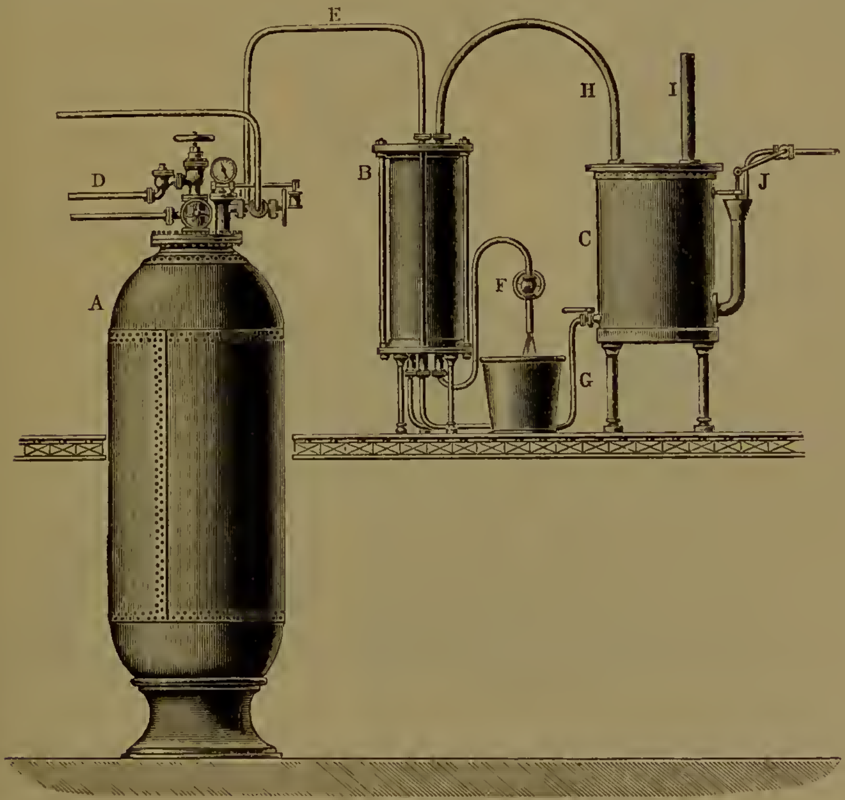

Fig. 70.

It has been shown above (p. 47) that saponification is accelerated by intimate contact of the reacting masses. In *Hughes'* autoclave this is obtained, as pointed out already, by a portion of the steam entering the autoclave under high pressure being allowed to escape continuously. In order to produce a more intimate intermixture *Michel*[1] designed the apparatus shown in Fig. 71. A pair of autoclaves is

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[1] English Patent, 8403, 1885; *Journ. Soc. Chem. Ind.* 1886, 432.

worked conjointly. They are charged through the pressure vessel A and pipe *l* with fat and water. The autoclaves are heated by fire, and as the pressure rises the contents of the autoclaves are forced up through the tubes *ff*, reaching almost to the bottom of the autoclaves, into the top of the mixing vessel C, whence the mass runs back again into the autoclaves. The mass, somewhat cooled in C, falls to the bottom of the autoclave through the hot mass therein, thus contributing to the thorough intermixing of fat and water. This play repeats itself whilst the pressure on the autoclaves is kept up at 15 atmospheres for eight hours. The hydrolysed mass is then forced through pipe *h* into the vessel D, in which separation into two layers

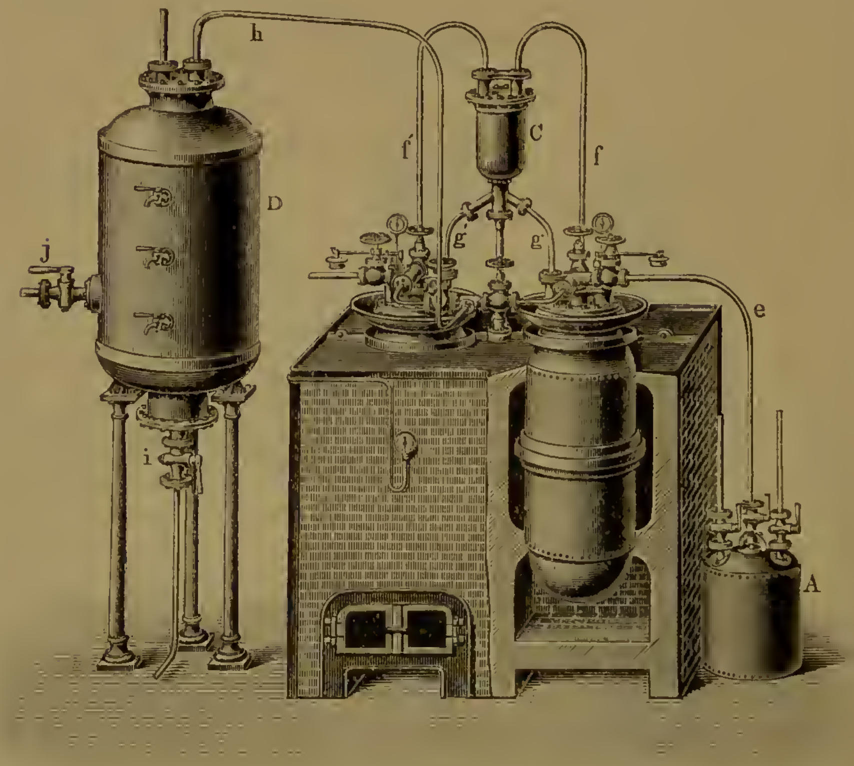

Fig. 71.

—an upper layer of fatty acids and a lower layer of glycerin water ("sweet water")—takes place. The heating of the autoclave by direct fire is, however, a serious drawback of the process, as this possibly may lead to burning of the fat. Therefore, *Michel's* method is less acceptable than *Hughes'*. The autoclaves were shown at the Paris Exhibition of 1889, but, as far as the writer is aware, the process has not been adopted in Europe.

Since the pressure and the temperature of steam stand in a definite relation to each other, it follows that high pressure steam may be replaced by superheated steam standing under ordinary pressure. Hence hydrolysis should become feasible by treating fats with superheated steam at a sufficiently high temperature. A process based on the hydrolysis by means of steam under the ordinary pressure was patented as early as in the year 1825,[1] but it did not gain practical importance until *Wilson* and *Payne*[2] took their patent for "Improvements in distilling fatty and oily matters." In their process glycerides were heated in a still, whilst superheated steam was sent through the fatty mass, the temperature of which was kept between 550° and 600° F. The products of hydrolysis, viz. the fatty acids and glycerol, were carried over by the water vapours. The apparatus employed was similar to the one illustrated in Fig. 80. Although this process was worked for a number of years it had been abandoned, since considerable quantities of fatty matter underwent destruction. *Lewkowitsch*[3] endeavoured to render practicable this mode of hydrolysing by heating the fats in a current of superheated steam *in vacuo.* Also this process proved unremunerative, and has therefore been abandoned.

The products of hydrolysis obtained in *Hughes'* and *Michel's* processes are treated in the same manner as those obtained in the following processes:—

(2) AQUEOUS SAPONIFICATION WITH THE ASSISTANCE OF BASES

The chemical reaction symbolising the saponification of fats by means of bases has been given on p. 52 [equation (4)]. It has also been shown there that in order to effect complete saponification in an open vessel, a larger quantity of bases is required than theory demands. Indeed, if lime be used, the proportion of caustic lime—CaO—must be 12 to 14 per cent instead of the theoretical quantity of 9·7 per cent (p. 52).

The technical process based on the saponification by means of 12-14 per cent of lime and leading to the conversion of the total fatty acids into lime soaps is due to *De Milly.* The fat is churned up with water in an open, lead-lined vat by means of live steam sent into the emulsion through an open coil; whilst the mass is kept in ebullition, caustic lime previously slaked and made into a thin cream is gradually introduced. The boiling is kept up until the saponification is completed, the outward sign of which is readily recognised by the lime soap separating from the water. The glycerin water—"sweet water"—can then be run off, and the still soft lime soap washed to remove occluded glycerol and decomposed with sulphuric acid. In the older methods the lime soap was allowed to cool, when it settled as a hard mass—"rock"—from which the supernatant glycerin solution was run off. This hard lime soap was then washed and reduced to powder by grinding or decomposed with sulphuric acid, when the calcium was precipitated as sulphate, whilst the liberated fatty acids rose to the top as a clear oily layer.—The fatty acid and the glycerin—"sweet

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[1] English Patent, 5183, 1825.

[2] English Patent, 1624, 1854.

[3] English Patent, 5985, 1888.

water"—are worked up for candle material and crude glycerin, as will be described below.

The large amount of lime (and consequently the large amount of sulphuric acid) required in this process renders it a very costly one, so that it has been largely superseded by methods of saponification under pressure (see below). Still, the simple and inexpensive installation required for it, and the ease with which the operation can be carried out, combined with the fact that the fatty acids so obtained yield the best and purest candle material, have been instrumental in keeping this process alive, especially so in small works. In large establishments, however, economical reasons render a reduction of the bases and of the acid imperative. Such reduction is possible through treating the fats with milk of lime in an autoclave under pressure.

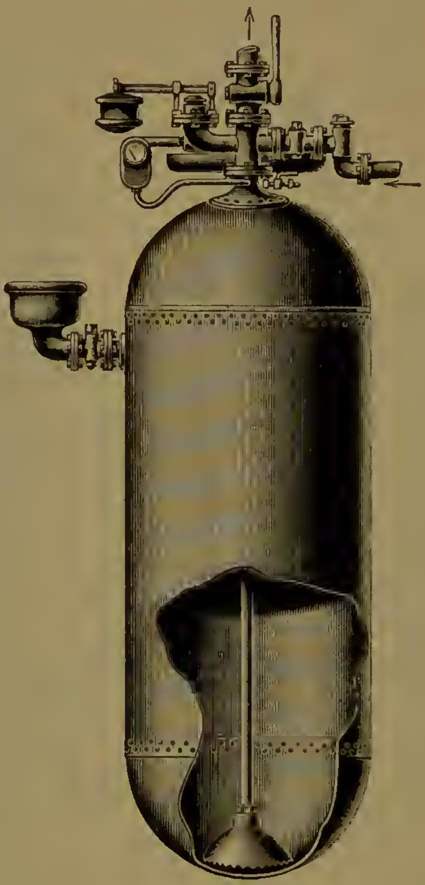

Fig. 72.

It has been shown above (page 52) that as the pressure rises the amount of bases may be reduced, the bases merely acting as accelerators. Hence the greater the pressure the less of the bases need be used.

In the modern practice of candle works autoclaves are therefore worked at a pressure of about eight atmospheres (=120 lbs. per square inch). At this pressure the fat is practically completely hydrolysed when employing about 3 per cent of lime on the fat. The autoclaves in use are illustrated by Figs. 72 and 73. The autoclave shown in Fig. 72 consists of a cylindrical vessel made of copper, strong enough to withstand a working pressure of eight atmospheres, and provided with an internal steam pipe which reaches the bottom of the vessel. In Fig. 72 the steam leaves at the bottom of the serrated cone, and is thus divided into a number of streamlets which churn the mixture of fat and water into a thorough emulsion. The water and fat, in the proportions of 1 to 3 or 1 to 4, as also the milk of lime, are fed through the funnel-shaped vessel at the side of the autoclave.

The following tables will be found to render some assistance to the works' chemist :—

Milk of Lime in Degrees Baumé obtained from 1 *Kilogram of Caustic Lime*

1 Kilogram Caustic Lime yields Milk of Lime of		Weight of Milk of Lime.	1 Kilogram Caustic Lime yields Milk of Lime of		Weight of Milk of Lime.
Degrees Baumé.	Liters.	Kilograms.	Degrees Baumé.	Liters.	Kilograms.
10	7·50	9·44	38	3·39	5·07
11	7·10	9·01	39	3·37	5·05
12	6·70	8·60	40	3·35	5·03
13	6·30	8·20	41	3·34	5·01
14	5·88	7·80	42	3·32	5·00
15	5·50	7·43	43	3·31	4·98
16	5·25	7·16	44	3·30	4·96
17	5·01	6·92	45	3·29	4·95
18	4·80	6·70	46	3·28	4·93
19	4·68	6·51	47	3·27	4·92
20	4·42	6·38	48	3·26	4·90
21	4·24	6·18	49	3·25	4·89
22	4·16	6·05	50	3·24	4·88
23	4·05	5·92	51	3·23	4·87
24	3·95	5·81	52	3·220	4·86
25	3·87	5·72	53	3·215	4·85
26	3·81	5·63	54	3·210	4·84
27	3·75	5·56	55	3·205	4·83
28	3·70	5·49	56	3·200	4·82
29	3·65	5·43	57	3·195	4·81
30	3·60	5·36	58	3·190	4·800
31	3·56	5·31	59	3·185	4·795
32	3·52	5·27	60	3·180	4·790
33	3·49	5·22	61	3·175	4·780
34	3·47	5·19	62	3·170	4·775
35	3·45	5·16	63	3·165	4·770
36	3·43	5·13	64	3·160	4·760
37	3·41	5·10	65	3·150	4·750

Percentages of Caustic Lime in Milk of Lime

Degrees Baumé.	Per cent.	100 Liters contain Kilograms CaO.	Degrees Baumé.	Per cent.	100 Liters contain Kilograms CaO.
10	10·60	13·3	38	19·72	29·5
11	11·12	14·2	39	19·80	29·6
12	11·65	15·2	40	19·88	29·8
13	12·16	16·1	41	19·95	29·9
14	12·68	17·0	42	20·03	30·1
15	13·20	18·0	43	20·10	30·2
16	13·72	18·9	44	20·16	30·3
17	14·25	19·8	45	20·22	30·4
18	14·77	20·7	46	20·27	30·5
19	15·23	21·6	47	20·32	30·6
20	15·68	22·4	48	20·37	30·7
21	16·10	23·3	49	20·43	30·7
22	16·52	24·0	50	20·48	30·8
23	16·90	24·7	51	20·53	30·9
24	17·23	25·3	52	20·57	31·0
25	17·52	25·8	53	20·62	31·1
26	17·78	26·3	54	20·66	31·1
27	18·04	26·7	55	20·70	31·2
28	18·26	27·0	56	20·74	31·3
29	18·46	27·4	57	20·78	31·3
30	18·67	27·7	58	20·82	31·4
31	18·86	27·9	59	20·85	31·4
32	19·02	28·2	60	20·89	31·5
33	19·17	28·4	61	20·93	31·5
34	19·31	28·7	62	20·97	31·6
35	19·43	28·9	63	21·00	31·6
36	19·53	29·1	64	21·03	31·7
37	19·63	29·3	65	21·05	31·7

Sulphuric Acid required to saturate 100 *Kilograms of Lime*

Degrees Baumé.	Containing Acid of 60° Baumé. Per cent.	Kilograms Acid required for 100 Kilograms CaO.	Kilograms Water to be added to 100 Kilograms Acid to obtain Acid of Degrees Baumé.				
			5° B.	10° B.	15° B.	20° B.	25° B.
66	100·0	175·0	2477	1318	831	554	400
65	97·04	180·3	2471	1313	826	548	395
64	94·10	186·0	2465	1303	820	543	389
63	91·16	196·5	2455	1297	810	532	380
62	88·22	198·4	2451	1294	807	529	376
61	85·28	205·2	2446	1288	801	525	370
60	82·24	212·5	2439	1280	794	516	362
59	80·72	216·8	2434	1276	789	512	358
58	79·12	221·2	2430	1272	785	508	354
57	77·52	226·0	2425	1267	780	503	349
56	75·92	230·5	2421	1263	775	498	344
55	74·32	235·4	2416	1255	770	494	339
54	72·70	240·7	2411	1252	765	488	334
53	71·17	245·9	2405	1247	760	481	328
52	69·30	252·5	2399	1241	754	476	322
51	68·05	257·2	2494	1235	748	471	318
50	66·49	263·3	2386	1230	743	465	314
49	64·37	271·9	2379	1222	734	457	303
48	62·80	278·7	2372	1214	727	450	297
47	61·32	285·4	2366	1208	721	443	289
46	59·85	292·4	2359	1201	714	436	272
45	58·05	302·0	2340	1188	704	427	273

When the autoclave is charged, steam is turned on and the vessel kept at a pressure of eight atmospheres for about eight to ten hours.

The progress of saponification is controlled by drawing samples from time to time, and ascertaining the amount of free fatty acids, in the manner illustrated by the example given on page 403. It should be noted that the samples contain lime soap, and that it is therefore necessary to boil the sample with dilute sulphuric acid so as to obtain a mixture of neutral fat and free fatty acids.

The following table illustrates the sampling of tallow saponified in an autoclave with 3 per cent of lime, at a pressure of eight atmospheres :—

Sample taken	after the	1st	hour	contained	38·55	per cent	free fatty acids.
,,	,,	2nd	,,	,,	77·40	,,	,,
,,	,,	3rd	,,	,,	83·9	,,	,,
,,	,,	4th	,,	,,	87·5	,,	,,
,,	,,	5th	,,	,,	88·6	,,	,,
,,	,,	6th	,,	,,	89·3	,,	,,
,,	,,	7th	,,	,,	93·0	,,	,,
,,	,,	8th	,,	,,	97·5	,,	,,
,,	,,	9th	,,	,,	98·1	,,	,,
,,	,,	10th	,,	,,	98·6	,,	,,

Fig. 73.

Another form of an autoclave is shown in Fig. 73 ; the agitation effected by steam is assisted by a mechanical stirring arrangement.

A horizontal form of autoclave fitted with a stirring arrangement of a different kind is illustrated by Fig. 74.

Since the cylindrical autoclaves are liable to be bulged out by the high pressure, they would at last, if the bulging took place progressively in a regular manner, assume the shape of a sphere. Hence also spherical autoclaves (first suggested by *L. Bottaro* of Genoa) are in vogue. An autoclave of this kind, provided with a stirring arrangement, is shown in Fig. 75.

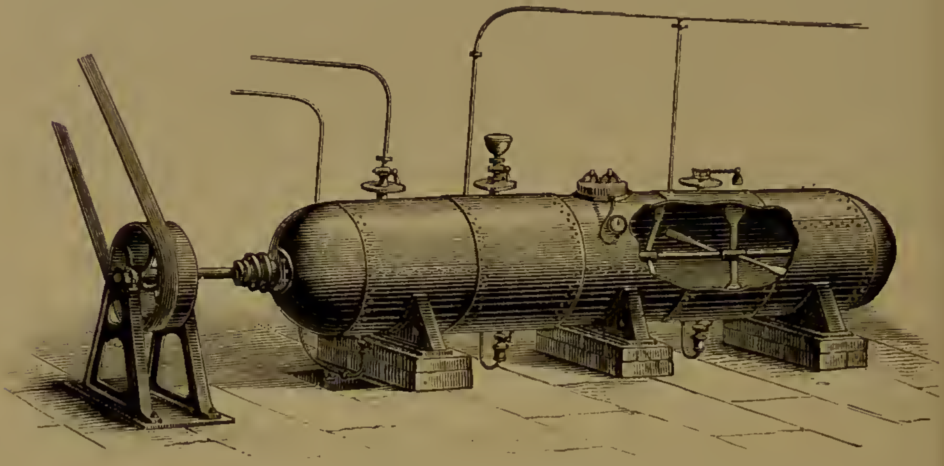

Fig. 74.

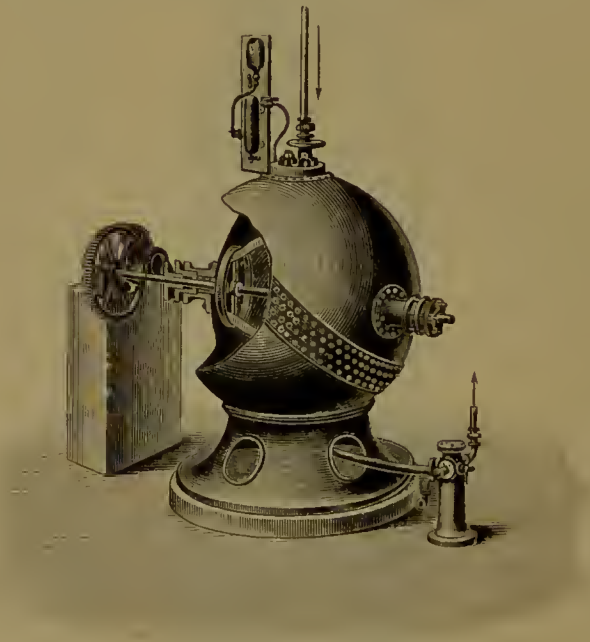

Fig. 75.

In the processes considered here the saponification reaches as high a figure as 98 to 99 per cent. When the saponification is deemed to be complete, the saponified mass is allowed to stand in the autoclave until it has separated into two layers: glycerin water—"sweet water"—and an upper layer of fatty acids, containing as much lime soap as corresponds to the lime introduced into the autoclave. These two layers are either pumped separately into store vats, or, in order to save time, the whole mass may be pumped into a settling vat, where the separation into the two layers takes place. The further working up of the glycerin solution into "saponified crude glycerin" will be considered under the heading "Glycerin," p. 1084. The fatty layer is boiled up with steam, and sufficient sulphuric acid is added to decompose the lime soap. On allowing to stand, the calcium sulphate separates out at the bottom of the aqueous layer, whereas the fatty acids form a clear oily layer on the top.

According to the fatty material employed, the composition of the fatty acids will naturally vary. The chief materials employed hitherto, at any rate in this country, in the saponification processes described above, being tallow and palm oil, or a mixture of both, it may be taken that the fatty acids consist approximately of 50 per cent of solid acids and 50 per cent of oleic acid. On the Continent also bone fat is largely "autoclaved" for candle-making purposes. The employment of palm oil is somewhat restricted, and other vegetable fats—such as vegetable tallow, shea butter, mowrah seed oil—are in use. The commercial exploitation of the large stores of suitable vegetable fats for the candle industry has, however, not yet attracted such attention from importers as this subject deserves.[1]

Since the oleic acid is useless as a candle material, the next operation is to effect its separation from the mixed fatty acids by pressure. The mixed fatty acids, after being thoroughly freed from mineral acid, are run into shallow trays arranged in tiers, in which the fatty acids are allowed to crystallise. The temperature at which the crystallisation takes place is carefully regulated, so as to obtain well-formed crystals of stearic and palmitic acids embedded in the mother liquor of oleic acid. If the fatty acids are cooled too rapidly, they solidify to an amorphous mass, from which it is extremely difficult to satisfactorily express the oleic acid ("spueing"). The solidified mass is taken out of the trays and pressed, at first at the ordinary temperature in a cold press, such as shown in Fig. 76. The bulk of the oleic acid—"red oil"—is thereby removed. The hard cakes still contain too much oleic acid, and are therefore expressed for a second time, at a somewhat higher temperature, in a hot press (Fig. 77), the cakes being placed in a bag of horse-hair, or other suitable material, between two press plates which are heated by live steam. In the figure shown the steam is supplied from above; but since the stuffing-boxes, owing to the wear and tear to which they are subjected, require frequent renewing, in more modern presses the steam is supplied from below.

The cakes are allowed to stand under pressure in the hot until a sufficient amount of oleic acid has been expressed to leave the cakes white, ready to be melted (after a further purification if

---

[1] Cp. Lewkowitsch, Cantor Lectures, *Journ. Soc. Arts*, 1904.

required) and to be moulded into candles. The oleic acid which runs from the hot-pressed cakes contains a considerable amount of solid acids—"stearine." These are recovered on the large scale, either by admixing the expressed material to the original fatty acids, or by treating it together with the "red oil" in the refrigerating plant.

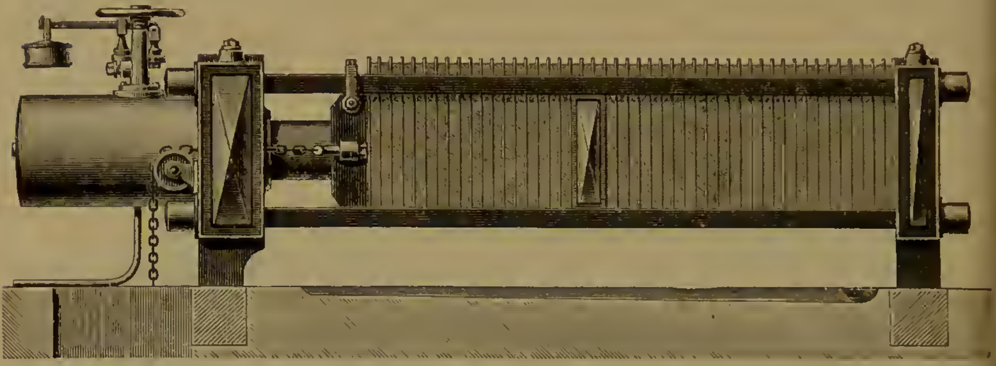

Fig. 76.

The amount of oleic acid in the cold-pressed (or hot-pressed) cakes is most rapidly determined by ascertaining the iodine value of the material. In this manner the pressing operations are readily controlled. (It should be noted that the expressed "oleine" contains most of the neutral oil which has escaped saponification in the autoclave process). For rapidly converting the iodine values into percentages of oleic acid, the following table, calculated by *Mangold*, may be found useful in the works' laboratory. The "stearine" of the table represents a mixture of palmitic and stearic acids.

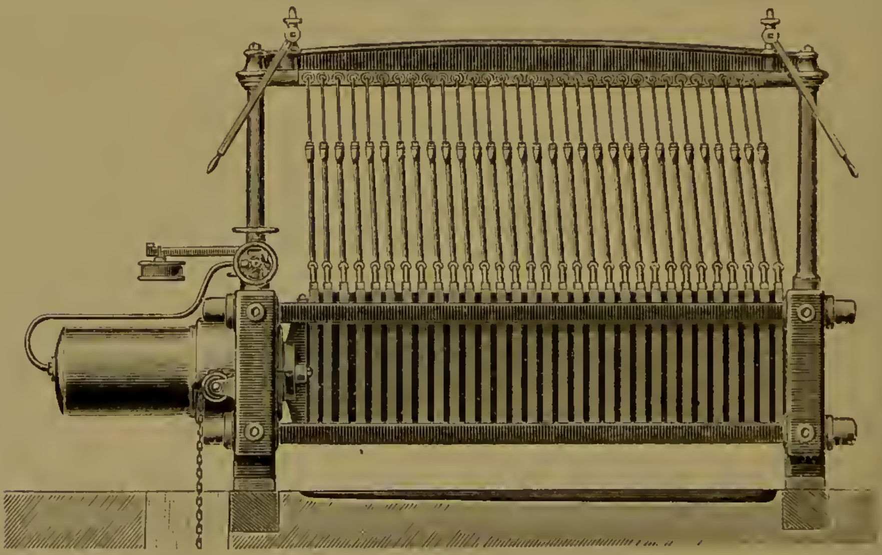

Fig. 77.

Iodine Value.	Product contains.		Iodine Value.	Product contains.		Iodine Value.	Product contains.	
	Oleic acid. Per cent.	"Stearine." Per cent.		Oleic acid. Per cent.	"Stearine." Per cent.		Oleic acid. Per cent.	"Stearine." Per cent.
0	0	100	31	34·41	65·59	62	68·83	31·17
1	1·11	98·89	32	35·52	64·48	63	69·94	30·06
2	2·22	97·78	33	36·63	63·37	64	71·05	28·95
3	3·33	96·67	34	37·74	62·26	65	72·16	27·84
4	4·44	95·56	35	38·85	61·15	66	73·27	26·73
5	5·55	94·45	36	39·96	60·04	67	74·38	25·62
6	6·66	93·34	37	41·07	58·93	68	75·49	24·51
7	7·77	92·23	38	42·18	57·82	69	76·60	23·40
8	8·88	91·12	39	43·29	56·71	70	77·71	22·29
9	9·99	90·01	40	44·40	55·60	71	78·82	21·18
10	11·10	88·90	41	45·51	54·49	72	79·93	20·07
11	12·21	87·79	42	46·62	53·38	73	81·04	18·96
12	13·32	86·68	43	47·73	52·27	74	82·15	17·85
13	14·43	85·57	44	48·84	51·16	75	83·26	16·74
14	15·54	84·46	45	49·95	50·05	76	84·37	15·63
15	16·65	83·35	46	51·06	48·94	77	85·48	14·52
16	17·76	82·24	47	52·17	47·83	78	86·59	13·41
17	18·87	81·13	48	53·28	46·72	79	87·70	12·30
18	19·98	80·02	49	54·39	45·61	80	88·82	11·18
19	21·09	78·91	50	55·50	44·49	81	89·93	10·07
20	22·20	77·80	51	56·62	43·38	82	91·04	8·96
21	23·31	76·69	52	57·73	42·27	83	92·15	7·85
22	24·42	75·58	53	58·84	41·16	84	93·26	6·74
23	25·53	74·47	54	59·95	40·05	85	94·37	5·63
24	26·64	73·36	55	61·06	38·94	86	95·48	4·52
25	27·75	72·25	56	62·17	37·83	87	96·59	3·41
26	28·86	71·14	57	63·28	36·72	88	97·70	2·30
27	29·97	70·03	58	64·39	35·61	89	98·81	1·19
28	31·08	68·92	59	65·50	34·50	90·07	100	0
29	32·19	67·81	60	66·61	33·39			
30	33·30	66·70	61	67·72	32·28			

A more direct method of carrying out the valuation of the solid acids is to determine their solidifying point.

Y. de Schepper and *Geitel*[1] recommend each candle-works' chemist to construct an empirical table for his own use, from which the yield of candle material can be found at a glance. It goes without saying that a table of this kind holds good only for the particular works for which it is constructed, as the solidifying points of the mixed fatty acids and the yields of candle material naturally vary considerably under varying conditions.

The following table, due to *de Schepper* and *Geitel*, affords the necessary guidance (cp. also table, p. 1024):—

---

[1] *Dingl. Polyt. Journ.* 245, 295.

[Table

Solidifying Point of the Mixture.	Stearine of Solidifying Point 48° C.	Solidifying Point of the Mixture.	Stearine of Solidifying Point 48° C.	Solidifying Point of the Mixture.	Stearine of Solidifying Point 48° C.
°C.	Per cent.	°C.	Per cent.	°C.	Per cent.
5·4	...	20	12·1	35	39·5
6	0·3	21	13·2	36	43·0
7	0·8	22	14·5	37	46·9
8	1·2	23	15·7	38	50·5
9	1·7	24	17·0	39	54·5
10	2·5	25	18·5	40	58·9
11	3·2	26	20·0	41	63·6
12	3·8	27	21·7	42	68·5
13	4·7	28	23·3	43	73·5
14	5·6	29	25·2	44	78·9
15	6·6	30	27·2	45	83·5
16	7·7	31	29·2	46	89·0
17	8·8	32	31·5	47	94·1
18	9·8	33	33·8	48	100·0
19	11·1	34	36·6		

Such an empirical table is computed by mixing the finished product "stearine" and the finished oleic acid as manufactured in the works in known proportions, and determining the solidifying points of these mixtures. Of course a separate table must be constructed for each kind of fat or mixture of fats.

If the amount of stearic acid in the material be required, its proportion is ascertained by *Hehner and Mitchell's* method (cp. chap. viii. p. 354).

The "stearine" contained in the "red oil" (and in the runnings from the hot press) is recovered in the refrigerating plant by cooling the oleic acid. Various appliances are in vogue. The simplest plan is to refrigerate the oil in large tanks by brine or calcium chloride solution cooled in an ice machine and passed through a row of coils contained in the tank. The process requires attention, as the success of the operation depends on the formation of crystals which are separated from the oleic acid by means of a filter press.

A more rapid method of cooling consists in allowing the oil to run over a refrigerated wheel—*Petit's* wheel, Fig. 78. This is shown partly in section. The cooled brine enters at C, runs along the circumference of the wheel, and leaves at the opposite side. The oleine is fed into trough *f*, into which the rotating wheel dips, carrying with it upwards a thin film of oleic acid, which is thus rapidly cooled and deposits crystals of "stearine." The crystalline mass on reaching the scraper *h* is scraped off and the sludgy mass collected in the cooled vessel F, from which it is pumped through pump P into a filter-press. The crystals are introduced as an intermediate product, at a suitable stage of the process, into the crude candle material.

In place of lime, also magnesia and zinc oxide are employed as accelerators. The advantages which magnesia and zinc oxide offer would lie in that they do not yield a precipitate on decomposing the autoclaved fatty matter with sulphuric acid. This advantage is, however, more than counterbalanced by the fact that hydrolysis is not so readily effected by means of magnesia, at any rate in the case of tallow and palm oil, as by means of lime. Experience gained on a large scale has shown that tallow, autoclaved with 3 per cent of magnesia under the same conditions as with 3 per cent of lime, is hydrolysed only to the extent of about 96 per cent. In order to reach as good a result as is obtained by means of lime, the working pressure or (and) the length of time must be increased, as will be readily gathered from the theoretical principles explained in Chapter II. This is indeed borne out by the experiments, due to *Kassler*,[1] given in the following table. They should be looked upon as a corollary to the table given above (p. 1011).

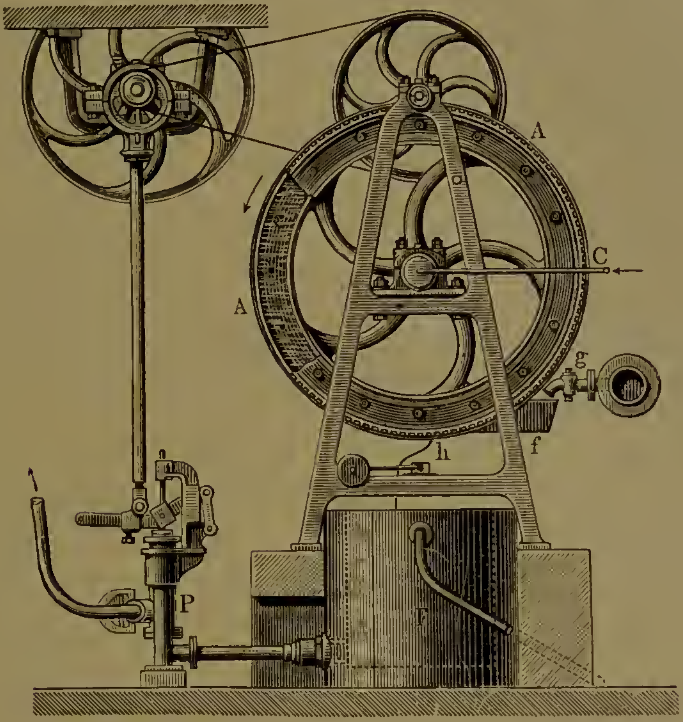

Fig. 78.

Saponification of Shea Butter with 3 per cent of Magnesia at a Pressure of 9 Atmospheres

	Free Fatty Acids. Per cent.	
	a	*b*
Sample taken after the 1st hour contained	61·4	63·2
,, ,, 2nd ,,	80·2	81·9
,, ,, 3rd ,,	90·2	90·1
,, ,, 4th ,,	91·1	94·8
,, ,, 5th ,,	95·4	95·7
,, ,, 6th ,,	95·5	97·1
,, ,, 7th ,,	96·6	97·1
,, ,, 8th ,,	98·1	98·0

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[1] *Augsb. Seifensieder Zeitung*, 1902, 312.

The pressure being higher than in the case of lime, discolouration of the fatty acids takes place to a somewhat greater extent, and the resulting "sweet water" is more dilute.

Zinc oxide does not offer these disadvantages, but its higher cost does outweigh the benefit derived from its use. A small percentage of zinc oxide or of zinc dust is, however, frequently used conjointly with lime, as the discolouration of the fatty acids is thereby somewhat diminished (cp. "Soap Manufacture," p. 1068).

Yield of the Process. The yield of candle material by the autoclave process depends, of course, on the melting points of the finished stearine, and on the completeness with which the "stearine" is recovered from the oleic acid. It may, however, be taken as sufficiently accurate that the amount of high melting point "stearine" from tallow or palm oil, or a mixture of both, varies from 45 to 47 per cent of the raw material, about 30 per cent being obtained from the hot press and the remainder from the refrigerated oleic acid. The finished oleic acid, "oleine," amounts to 47 to 48 per cent. In the case of good tallow, the yield of "saponification crude glycerin" of specific gravity 1·240 reaches 10 per cent. This is summarised in the following table:—

Yield from 100 parts of Tallow by the Autoclave Process.

Candle material (stearic and palmitic acids)	45 - 47	parts
Oleic acid (containing unsaponified fat	48 - 47	,,
Glycerin	10 - 10	,,
	103-104	,,

The "stearine" is used either as such, or in admixture with paraffin wax, etc. (see below), as candle material. The oleic acid, "oleine," is either converted into textile soap or used as a wool oil (cp. p. 954). In the mixed process (see below) part of the oleic acid is converted into candle material.

The production of "saponification crude glycerine" from the "sweet water" will be described under "Glycerin."

If the fatty acids obtained by the autoclave process be too dark, and hence do not yield sufficiently white candle material, they must be purified by distillation. This is carried out in the same apparatus as is described under acid saponification, and in the same manner as is detailed under "Mixed Process."

In the distilling process the fatty acids do not undergo a chemical change (cp. p. 71), provided due care be observed in conducting the distillation. Since, however, the autoclaved mass contains some small proportion of unsaponified fat, which goes on accumulating in the still—especially if the still be fed continuously—decomposition of the unsaponified fat finally takes place with formation of hydrocarbons (destructive distillation, p. 19).

Kassler[1] has shown that if during the progress of distillation so much neutral fat has accumulated that its proportion amounts to 12 to 15 per cent of the still contents, hydrocarbons are formed. (In the case of autoclaved bone fat fatty acids, small amounts of hydrocarbons appear at the outset of the distillation.) Hence those portions of the distillate which are caught towards the end of the "run" are collected separately ("Still Returns") and redistilled.

In the following table I have compiled a number of large scale experiments made by *Kassler*[2] with several kinds of fatty acids. The neutral fats had been hydrolysed in an autoclave with 2·6-3 per cent of magnesia at a pressure of 9 atmospheres; the autoclaved mass was freed from magnesia by dilute sulphuric acid :

Yield from Autoclaved Fatty Acids on Distillation

No.	From	Quantity Distilled.	Duration of Distillation.	Distillate for Presses.	"Still Returns."	"Stearine Pitch."
		Tons. about	Hours.	Per cent.	Per cent.	Per cent.
1	Tallow stearine .	8	36	95·6	2·1	2·3
2	Vegetable tallow	5	35	92·4	4·0	3·6
3	Tallow . .	5	36	94·2	2·3	3·5
4	Bone fat . .	5	38	91·5	5·0	3·5
5	Palm oil . .	5	37	91·3	4·5	4·2
6	Shea butter .	5·3	29	94·1	2·4	3·7

In the following table, due to *Kassler*,[3] are recorded the solidifying points and iodine values of the distillates, as obtained from hour to hour, during a "run":—

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[1] *Chem. Revue*, 1903, 151.

[2] *Chem. Revue*, 1902, 49 ; *Augsburger Seifensieder Zeitung*, 1902, 311, 329.

[3] *Augsburger Seifensieder Zeitung*, 1902, 349.

[TABLE

Distillation of Autoclaved Fatty Acids

Samples taken after Hours.	Tallow Acids of Solidifying Point 41·7 °C., containing: Oleic Acid, 41·5 per cent; Neutral Fat, 3·6 per cent.			Bone Fat Acids of Solidifying Point 39·8 °C., containing: Oleic Acid, 60·4 per cent; Neutral Fat, 2·5 per cent.			Palm Oil Acids of Solidifying Point 41·6 °C., containing: Oleic Acid, 60·4 per cent; Neutral Fat, 2·9 per cent.			Shea Butter Acids of Solidifying Point 48·4 °C., containing: Neutral Fat, 2 per cent.		
	Solidifying Point.	Oleic Acid.	Hydrocarbons.	Solidifying Point.	Oleic Acid.	Hydrocarbons.	Solidifying Point.	Oleic Acid.	Hydrocarbons.	Solidifying Point.	Iodine Value.	Hydrocarbons.
	°C.	Per cent.	Per cent.	°C.	Per cent.	Per cent.	°C.	Per cent.	Per cent.	°C.	Per cent.	Per cent.
5	40·4	38·0	...	37·2	54·9	...	43·8	56·0	...	48·9	47·24	...
6	40·4	38·3	...	38·1	54·9	...	43·8	56·2	...	49·7	47·72	...
7	40·7	38·9	...	38·1	55·7	...	43·8	56·3	...	50·5	48·05	...
8	40·9	38·9	...	38·3	56·2	...	43·5	56·7	...	50·4	48·04	...
9	41·2	39·5	...	38·7	56·5	...	43·4	56·9	...	49·8	48·37	...
10	41·3	39·9	...	38·8	57·0	...	43·1	57·6	...	50·3	48·50	...
11	41·3	40·5	...	38·9	57·6	...	42·4	58·8	...	50·3	48·50	...
12	41·3	41·0	...	38·9	58·1	...	42·2	59·0	...	50·8	48·71	...
13	42·5	41·2	...	39·2	58·5	...	42·0	59·0	...	50·8	48·77	...
14	42·7	41·5	...	39·2	59·4	...	41·0	59·0	...	50·9	48·97	...
15	42·9	41·7	...	39·2	59·8	...	40·8	59·5	...	51·3	49·14	...
16	43·0	42·0	...	39·4	59·9	0·5	40·5	59·5	...	51·3	49·29	...
17	43·2	42·5	...	39·5	60·7	0·9	40·1	59·7	0·5	51·0	50·56	...
18	43·4	42·5	...	39·8	60·9	1·3	39·8	59·9	1·1	50·7	51·00	...
19	43·6	42·5	...	40·0	61·2	1·8	39·8	60·4	1·7	51·1	51·62	...
20	44·5	42·7	...	40·5	61·2	2·2	39·3	60·8	2·3	51·1	51·73	...
21	44·5	42·7	0·2	40·3	61·4	2·9	39·2	61·1	2·8	50·9	51·40	...
22	44·6	42·8	0·8	40·3	61·6	3·5	39·1	62·0	4·0	50·9	51·18	...
23	43·2	43·0	1·2	40·0	61·8	3·8	38·2	62·7	4·5	51·2	51·23	...
24	42·5	43·1	1·7	39·0	62·0	4·2	38·0	63·4	5·1	51·3	51·32	...
25	40·0	43·0	2·9	39·0	62·1	4·5	38·0	63·8	5·1	51·3	51·42	0·34
26	...	...	...	...	...	...	...	...	...	51·4	51·59	0·78
27	...	...	...	...	...	...	...	...	...	51·5	51·68	0·92
28	...	...	...	...	...	...	...	...	...	51·3	51·79	2·80
29	...	...	...	...	...	...	...	...	...	51·3	51·64	3·56
30	...	...	...	...	...	...	...	...	...	50·8	51·52	5·07

(3) Sulphuric Acid Saponification, Hydrolysis by means of Concentrated Sulphuric Acid

The theory of this method of hydrolysis has been discussed already in Chapter II. The technical process consists in rapidly intermixing fat, previously heated to a temperature of about 120° C. and thereby freed from the last traces of moisture, with 4 to 6 per cent of concentrated sulphuric acid of 66°-67° Baumé. If sulphuric acid of lower strength be used the hydrolysis is not complete, as will be gathered from the table given on page 44. With the decrease of strength of sulphuric acid the hydrolysis decreases, until with acids of 60 per cent of SO_4H_2 hydrolysis no longer takes place.

The action of sulphuric acid on the saturated glycerides is of little practical importance, since the sulphonated compounds (of the glycerides as well as of the saturated fatty acids) are subsequently decomposed, yielding the saturated acids practically unchanged. With olein, however (the less saturated glycerides need not be considered here, as being of no practical importance in the manufacture of "Stearine"), the sulphuric acid forms saturated sulphonated compounds, a small quantity of sulphurous acid being at the same time evolved in consequence of secondary reactions taking place. These sulphonated compounds have the property of being somewhat readily hydrolysed on boiling with water (cp. tables pp. 43 and 44).

The higher the temperature to which the fat has been heated, and the larger the percentage of sulphuric acid used, the more copious is the evolution of sulphurous acid and the further will the secondary reactions proceed. In order to reduce the destruction (carbonising) of organic matter, leading to a lower yield of fatty acids, and especially of glycerol, great attention must be paid to the following factors:—Quantity of sulphuric acid, temperature, and time of contact of the acid with the fat. In order to ensure the most intimate contact with the conc. acid within the shortest possible time, various mixing machines are used. One apparatus is shown in Fig. 79. Other devices consist in pulverising the fatty matter by centrifugal force, etc.

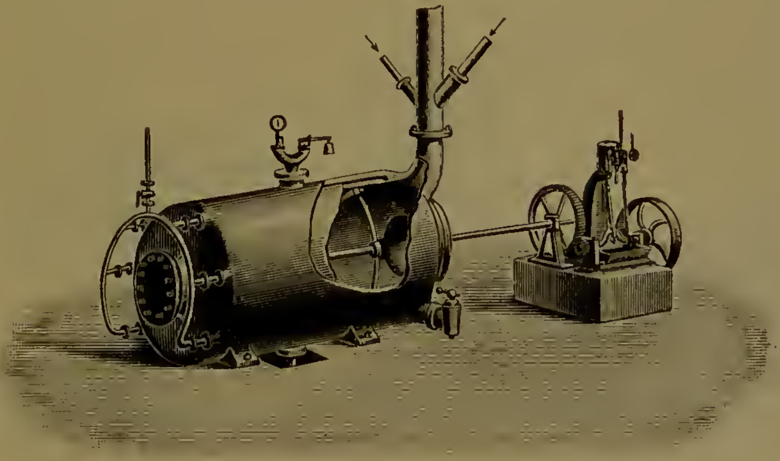

Fig. 79.

The sulphonated mass is next run into boiling water and agitated by steam until the sulphonated compounds are hydrolysed. The mass is then allowed to stand, when separation into two layers takes place: a lower aqueous layer containing the sulphuric acid employed as also the glycerol, and an upper layer of fatty material.

This fatty material is as a rule so dark that it cannot be pressed immediately after solidifying in the manner described under (2). In order to obtain material of good colour the fatty mass must be distilled. A type of apparatus employed for this purpose is shown in Fig. 80.

The fatty material, thoroughly freed from mineral acid by washing with water, is charged into still A, where it is heated at first by direct fire. When the material is sufficiently hot, a current of steam, dried preliminarily in P and superheated in S, is introduced through P, and the fatty acids are thus carried over through D into the cooling worm R. The acids run into box X, where the separation from the condensed water takes place. The raw product is drawn off at Z; any vapours escape through G. The fatty material drawn off at Z represents a mixture of liquid acids and candle material, which is pressed in the cold and subsequently in the hot as described above (p. 1013).

In other installations lenticular stills are employed in order to diminish the height to which the fatty acids must rise; the condensing arrangement also is widely varied. In the plant shown in Fig. 80 the whole distillate is obtained in one mass. Some manufacturers collect the distillate in several fractions, whereby the subsequent separation into solid and liquid material is said to be somewhat simplified. The portions distilling over towards the end of the operation are so dark coloured and contaminated with impurities that they must be redistilled, hence they are termed "still returns" (German, *Blasenretourgang*). The distillation of such "still-returns" is exemplified by the second table, p. 1026.

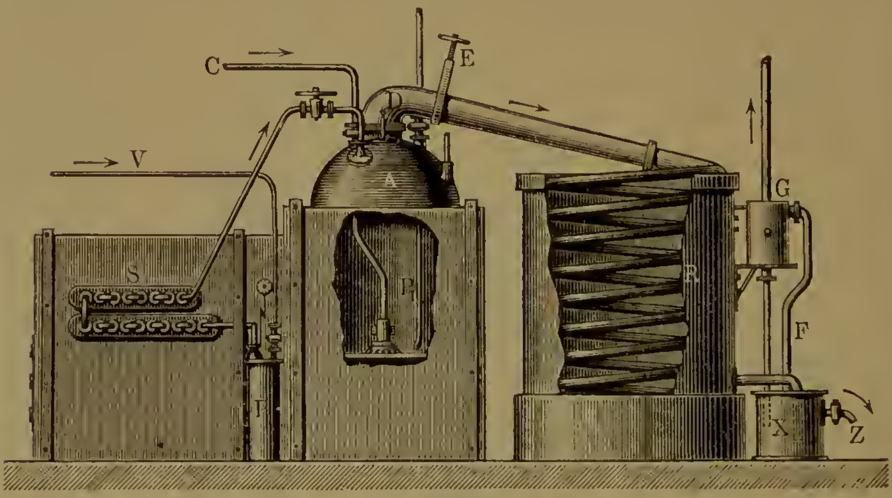

Fig. 80.

The acid saponification process leads to a greater yield of candle material than the autoclave process. Whereas the candle material obtained by the latter process amounts to 46 to 47 per cent (see p. 1018), the yield of "stearine" by sulphuric acid saponification is from 61 to 63 per cent, and that of oleic acid 30 per cent, as against 47 per cent from the autoclave process.

It is therefore evident that a certain amount of oleic acid has been converted into solid material. The chemical change taking place has already been incidentally explained on p. 105 and p. 121. Owing to the great technical importance of this chemical change, the conversion of oleic acid into candle material will be fully considered below (p. 1027). It may, therefore, suffice here to state that in the acid saponification process from 15 to 17 per cent of oleic acid are converted chiefly into stearolactone and iso-oleic acid, with which small quantities of β-hydroxystearic may be admixed.

The progress of hydrolysis of the acidified fat is best controlled in the manner illustrated by the table given on p. 43.

The examination of the press cakes (from the cold press as well as from the hot press) by means of the iodine absorption test obviously does not lead to the same information as is obtained in the case of autoclaved material, since iso-oleic acid also absorbs iodine. The pressing operations are therefore best controlled by the determination of the *solidifying point* with the help of an empirical table worked out for each kind of fat or mixtures of fat.

As an example, I give the following table due to *Y. de Schepper* and *Geitel*,[1] computed in the candle-works of Gouda (Holland) for tallow and palm oil. The first column contains the solidifying points of the various intermediate products up to the finished "stearine." The yields of "stearine" of the solidifying points recorded in the first column were obtained by pressing the hydrolysed mass at different temperatures.

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[1] *Dingl. Polyt. Journ.* 245, 295.

Solidifying Point.	Percentage of "Stearine" of Solidifying Point stated.							
	Palm Oil.				Tallow.			
°C.	48°	50°	52°	55·4°	48°	50°	52°	54·8°
5	...	...	...	...	...	...	...	...
10	4·2	3·6	3·3	2·6	3·2	2·7	2·3	2·1
15	10·2	9·8	7·8	6·6	7·5	6·6	5·7	4·8
20	17·4	15·0	14·4	11·0	13·0	11·4	9·7	8·2
25	26·2	22·4	19·3	16·2	19·2	17·0	14·8	12·6
30	34·0	30·5	26·6	22·3	27·9	23·2	21·4	18·3
35	45·6	40·8	35·8	29·8	39·5	34·5	30·2	25·8
36	48·5	43·2	38·0	31·8	42·5	36·9	32·5	27·6
37	51·8	45·5	40·3	33·6	46·0	40·0	34·9	29·6
38	55·5	48·8	42·6	35·8	49·5	42·6	37·5	32·0
39	59·2	51·8	45·6	38·2	53·2	45·8	40·3	34·3
40	63·0	55·2	48·6	40·6	57·8	49·6	43·5	37·0
41	66·6	58·7	52·0	43·0	62·2	53·5	47·0	40·0
42	70·5	62·2	55·2	45·5	66·6	57·6	50·5	42·9
43	74·8	66·0	58·8	48·5	71·8	62·0	54·0	46·0
44	79·2	70·2	62·0	51·4	77·0	66·2	58·4	49·8
45	84·0	74·5	66·0	54·3	81·8	71·0	62·6	53·0
46	89·4	78·8	69·8	57·8	87·5	75·8	67·0	56·8
47	94·3	83·0	74·0	61·0	93·3	80·9	71·5	60·8
48	100·0	88·0	78·6	65·0	100·0	87·2	76·6	65·0
49	...	94·2	83·5	69·1	...	93·0	84·7	69·5
50	...	100·0	89·0	73·4	...	100·0	87·0	74·5
51	...	...	94·5	78·0	...	...	93·5	79·8
52	...	...	100·0	82·8	...	...	100·0	84·8
53	...	...	...	87·6	...	...	...	90·1
54	...	...	...	92·2	...	...	...	95·3
55	...	...	...	97·5	...	...	(54·8)	100·0
55·4	...	...	...	100·0	...	...	...	...

The stearine obtained by this process is known in commerce under the name "distilled stearine." This "stearine" has a somewhat lower solidifying point than "saponified stearine." Whereas the titer test of the latter is as a rule 132° F. to 134° F., the best commercial "distillation stearines" solidify at 129° F., or very little above this temperature.

The "distilled stearine" consists, therefore, of stearic, palmitic, iso-oleic acids, with which a small amount of hydroxystearic acid may be admixed, and of stearolactone. The amount of stearolactone may be inferred from the difference of the saponification and neutralisation values of the sample (cp. p. 339).

The proportion of iso-oleic acid can be calculated from the iodine value of the sample, oleic acid being assumed to be entirely absent.

The stearic acid is determined direct (p. 354). The presence of hydroxystearic acid is ascertained by determining the acetyl value (p. 276). The amount of palmitic acid is then found by difference.

The oleic acid resulting from this process is termed "distilled oleine," "distillation oleine" (cp. p. 1057).

The *crude glycerin* obtained (see p. 1021) is known as "distillation glycerin" (p. 1086); this term must, however, not be confounded with "distilled glycerine." The amount of the recovered crude glycerin is lower than in the autoclave processes. A definite figure cannot be given as the yield depends on the care exercised in the first stages of the process.

(4) THE MIXED PROCESS

From the above given notes regarding the yields of candle material and crude glycerin it will be gathered that more candle material is obtained in the "acid process" than by autoclaving the fatty materials, whereas a larger amount of glycerin of better quality results from the autoclave process. Hence a combination of these two processes suggests itself, for the action of sulphuric acid on olein is apparently the same as on oleic acid. The combined method, known as the "mixed process," consists in hydrolysing the material in an autoclave by means of bases, thus recovering the full amount of glycerin, and treating the fatty material with conc. sulphuric acid in the manner described under 3 (p. 1021). Any neutral fat which has escaped hydrolysis in the autoclave is thus saponified. Therefore, in the subsequent distillation of the acidified material less neutral fat accumulates in the still than is the case when autoclaved, non-acidified fatty acids are distilled. Hence the amount of hydrocarbons is also reduced. This will be gathered by comparing the following tables, due to *Kassler*,[1] with the corresponding table given p. 1019.

Yield from Autoclaved and Acidified Fatty Acids on Distillation

No.	From	Quantity Distilled.		Duration of Distilling.		Distillate for Presses.		"Still Returns."		"Stearine Pitch."	
		Tons.		Hours.		Per cent.		Per cent.		Per cent.	
		I.	II.	I.	II.	I.	II.	I.	II.	I.	II.
1	Tallow . .	5	7	34	33	94·8	94·6	2·0	2·6	3·2	2·8
2	Bone fat .	5	5·6	35	34	92·8	90·3	4·2	5·4	3·0	4·3
3	Palm oil .	5	5	36	32	91·6	91·0	4·6	5·3	3·8	3·7

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[1] *Augsburger Seifensieder Zeitung*, 1902, 349; *Chem. Rev.* 1902, 50.

Distillation of Autoclaved and Acidified Fatty Acids

Samples taken after Hours.	Tallow Acids of Solidifying Point 42·2 °C, containing: Oleic Acid, 29·8 per cent; Neutral Fat, 0·4 per cent.				Bone Fat Acids of Solidifying Point 40·4 °C., containing: Oleic Acid, 42·2 per cent.; Neutral Fat, 0·5 per cent.				Palm Oil Acids of Solidifying Point 42·8 °C., containing: Oleic Acid, 42·8 per cent.; Neutral Fat, 0·5 per cent.			
	Solidifying Point.	Oleic+Iso-oleic Acid.	Hydroxy-stearic Acid.	Hydrocarbons.	Solidifying Point.	Oleic+Iso-oleic Acid.	Hydroxy-stearic Acid.	Hydrocarbons.	Solidifying Point.	Oleic+Iso-oleic Acid.	Hydroxy-stearic Acid.	Hydrocarbons.
	°C.	Per cent.	Per cent.	Per cent.	°C.	Per cent.	Per cent.	Per cent.	°C.	Per cent.	Per cent.	Per cent.
5	41·7	33·1	4·0	...	37·8	50·3	5·9	...	45·9	51·2	6·0	...
6	41·9	33·8	4·3	...	37·9	51·1	6·0	...	45·9	51·5	6·0	...
7	42·2	34·4	4·5	...	38·3	51·5	6·3	...	46·0	52·4	6·3	...
8	42·5	35·0	4·7	...	38·3	51·9	6·3	...	45·8	52·4	7·0	...
9	42·7	35·7	5·5	...	38·3	52·3	6·8	...	44·8	53·3	7·5	...
10	42·7	36·1	5·5	...	38·3	53·0	8·0	...	44·2	53·8	7·5	...
11	42·7	36·6	5·8	...	38·4	53·4	8·2	...	43·8	54·2	5·0	...
12	43·0	36·9	5·8	...	38·5	53·8	8·3	...	42·9	54·7	4·2	...
13	43·0	37·7	6·0	...	39·5	54·2	8·3	...	42·7	54·8	3·0	...
14	43·3	38·3	6·3	...	39·6	54·7	6·2	...	41·8	55·8	2·8	...
15	43·5	38·8	5·9	...	39·7	55·7	6·0	0·3	41·0	56·5	2·8	...
16	43·8	39·1	5·7	...	39·9	58·6	3·2	0·5	41·0	57·2	2·8	...
17	44·1	39·6	5·7	...	40·0	58·6	3·0	0·9	40·8	58·0	1·0	0·2
18	44·4	40·4	5·0	...	40·2	59·1	2·2	1·1	40·5	59·1	...	0·3
19	44·6	40·8	3·7	0·2	40·2	59·3	1·4	1·3	40·1	59·9	...	0·5
20	45·0	41·3	3·3	0·5	40·5	59·7	0·5	1·5	39·8	60·7	...	0·5
21	45·2	41·5	3·0	0·7	40·7	60·4	...	1·9	39·8	61·5	...	0·6
22	45·2	42·2	1·1	0·7	40·8	60·9	...	2·2	39·3	61·6	...	0.8
23	45·8	42·2	...	1·2	41·0	61·5	...	2·7	39·0	61·9	...	2·0
24	45·0	42·4	...	1·3	40·8	61·5	...	3·0	38·8	63·0	...	2·2
25	42·7	42·5	...	1·8	39·9	61·8	...	3·6	38·8	63·0	...	2·7

The "still-returns" of Nos. 1 and 2 of table p. 1020, and of Nos. 1, 2, 3 of the last given table, were collected together and again distilled, with the following result (*Kassler*[1]):—

Distillation of "Still-Returns"

Quantity Distilled.	Duration of Distilling.	Distillate for Presses.	Second "Still-Returns" ("Green Oil").	Stearine Pitch.
Tons.	Hours.	Per cent.	Per cent.	Per cent.
2·5	23	77·2	17·0	5·8

The yield obtainable from neutral fats by the "mixed process" should therefore be—

Candle material	61 - 63	per cent.
Oleic acid	32 - 30	,,
Crude glycerin, 1·240	10 - 10	,,
	103-103	,,

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[1] *Chem. Revue*, 1902, 74.

Conversion of Oleic Acid into Candle Material

It has been shown that in the "acid saponification" process about 30 per cent of oleic acid are still obtained as a by-product. Since candle-making from "stearine" was introduced, numerous workers have endeavoured to convert oleic acid into a saturated acid, or at least into candle material, but hitherto the object has not been attained on a practical scale. This problem remains one of the most fascinating ones in the oils and fats industries, and is ever attracting the attention of the candle-maker.

In consideration of its importance this subject must be treated at some length. The earliest attempts were directed to the reduction of oleic acid into *stearic acid*. It has been pointed out above (p. 100), that whereas the lower members of the oleic acid series can be converted into saturated acids, oleic acid itself does not take up hydrogen.[1]

Oleic acid can be reduced to stearic acid by means of fuming hydriodic acid and phosphorus (p. 100), but as a commercial process this reaction is hopeless. By heating oleic acid with 1 per cent of iodine to 270°-280° C., *P. de Wilde* and *Reychler* succeeded in obtaining about 70 per cent of stearic acid. Moreover, only one-third of the iodine used could be recovered; hence also this process had to be abandoned (cp. p. 105). Even if the iodine was partly or wholly substituted by the cheaper bromine or chlorine, commercial failure resulted. The process had a fair trial on a large scale in a Belgian candle-works, but the large amount of valueless by-products, coupled with the fact that no material from which the autoclaves were made could resist the corrosive effect of the halogens, showed once more that beautiful laboratory experiments but too often lead to unfavourable results in large-scale operations.

The action of chlorine on oleic acid, and the reduction of the chloro-derivatives under pressure by means of zinc or iron powder has been made the subject of a German patent by *Zürrer*, who claims to have obtained solid saturated fatty acids.[2] Since, however, oleic acid is regenerated on reduction of monochlorostearic acid, as laboratory experiments show, this process cannot be a feasible one. Indeed, as far as the writer has been able to ascertain, this process has not been worked on a commercial scale.

I have carried out a number of experiments in a similar direction with bromo-derivatives of stearic acid, by converting oleic acid either into monobromostearic acid or dibromostearic acid, but on reducing the products by means of hydrogen no stearic acid could be obtained.

The conversion of oleic acid into *palmitic acid*, as indicated by *Varrentrapp's* reaction (p. 92), has been tried repeatedly on a large scale; lastly by *Radisson* in *Fournier's* works at Marseilles.[3] Although

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[1] Cp. Lewkowitsch, *On Attempts to convert Oleic Acid into Candle Material*, 1897, 390.

[2] German patent, 62,407, 1892.

[3] *Journ. Soc. Chem. Ind.* 1883, 98; 1884, 200.

candles made by this process were shown at the Paris Exhibition of 1878, they have disappeared from the market on account of their rank odour and their greasy touch. The writer ascertained [1] that the process had been abandoned not only for the reasons stated, but also on account of the high cost and the great danger attending the process in consequence of the evolution of hydrogen.

The conversion of oleic acid into *elaïdic acid* (p. 104), although frequently patented, does not lead to technically useful results. The conversion of oleic acid into elaïdic acid by means of nitrous acid is not a complete one, hence the purification of the crude elaïdic acid alone renders this process an unremunerative one. The change of oleic acid into elaïdic acid by means of sodium bisulphite is a reversible one, and therefore leads to a low yield of elaïdic acid. Moreover, even pure elaïdic acid is not a good candle material.

The action of *zinc chloride* on oleic acid with a view to converting it into solid material has been tried at temperatures of about 200° C. without commercial success. The study of the reaction has again been taken up by *M. v. Schmidt.* 10 parts of oleic acid were heated with 1 part of zinc chloride to exactly 185° C., until a sample after boiling with hydrochloric acid solidifies on cooling. The resulting product was then repeatedly boiled out first with hydrochloric acid, and finally with water. The crude product obtained by the interaction of zinc chloride and oleic acid had, according to *Benedikt*,[2] the following composition:—

	Per cent.
Liquid anhydride	8
Stearolactone	28
Oleic and iso-oleic acids	40
β-Hydroxystearic acid	22
Saturated fatty acids (by difference)	2
	100

In examining the process, I found on a laboratory scale no solid saturated acids other than hydroxystearic acid.[3] Recently *Shukoff* and *Schestakoff* stated that they never obtained more than 8-9 per cent of stearolactone.[4]

The crude product was distilled in a current of superheated steam, and the distillate separated by hydraulic pressure into candle material and oleic acid. The candle material thus prepared gave on analysis the following result:—

	Per cent.
Stearolactone	75·8
Iso-oleic acid	15·7
Solid fatty acids	8·5
	100·0

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[1] Technical Report on the Paris Exhibition, *Chem. Zeit.* 1889, 1190.
[2] Benedikt, *Monatshefte f. Chem.* 1890, 71; *Journ. Soc. Chem. Ind.* 1890, 658.
[3] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1897, 392.
[4] *Journ. f. prakt. Chem.* 1903, 418.

Schmidt's process has been tried on a large scale in an Austrian candle-works. The quantity of oleic acid that remains unattacked, and the considerable amount of liquid unsaponifiable substances formed was so great, that the process had to be abandoned.

Zinc chloride seems to act on oleic acid in a manner analogous to concentrated sulphuric acid (cp. also Polymerised Castor Oil, p. 969). Very likely two isomeric zinc chloride-addition compounds are formed, which are subsequently decomposed on boiling with dilute hydrochloric acid into zinc chloride and two isomeric hydroxystearic acids, one of which is changed into stearolactone with loss of one molecule of water.

At present the only practical process for the conversion of oleic acid into candle material rests on the interaction of sulphuric acid with oleic acid. *Geitel*[1] has shown that on dissolving oleic acid in cold concentrated sulphuric acid, stearic acid hydrogen sulphate is formed. On subsequently boiling the product with water, β-hydroxystearic acid and small quantities of stearolactone are obtained, and on distilling the mass in a current of steam, as is done on a large scale, the stearolactone passes over unchanged, whereas the β-hydroxystearic acid is converted into oleic and iso-oleic acids. Besides, liquid anhydrides are formed. This play of (partly reversible) reactions explains why, on working the sulphuric acid saponification on a large scale, out of the 47 per cent of oleic acid obtainable from tallow in the autoclave process (p. 1018), only 15-17 per cent are converted into candle material, 30 per cent of oleic acid still being obtained as a by-product.

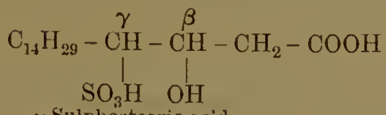
The rationale of the chemical action taking place when sulphuric acid acts on oleic acid in the cold may, perhaps, be explained as follows (*Lewkowitsch*[2]):—

In the first instance sulphuric acid is assimilated by oleic acid, much as bromine is absorbed by the latter, with formation of saturated products. But in the present case there is this important difference, that as the two groups SO_3H and OH are different, two products may be expected, according as the SO_3H group is assimilated by the β or the γ carbon atom,[3] thus—

$$C_{14}H_{29}-CH=CH-CH_2-COOH$$

Oleic acid.

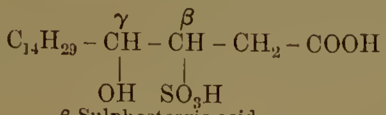
yields

(1) 

$$C_{14}H_{29}-\underset{SO_3H}{\overset{\gamma}{CH}}-\underset{OH}{\overset{\beta}{CH}}-CH_2-COOH$$

γ-Sulphostearic acid.

and

(2) 

$$C_{14}H_{29}-\underset{OH}{\overset{\gamma}{CH}}-\underset{SO_3H}{\overset{\beta}{CH}}-CH_2-COOH$$

β-Sulphostearic acid.

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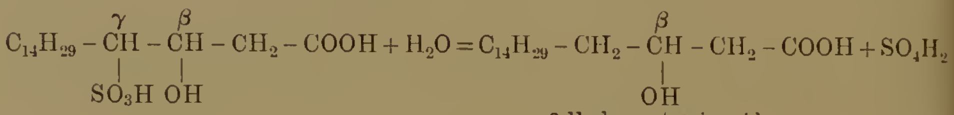
[1] Cp. p. 105.

[2] *Journ. Soc. Chem. Ind.* 1897, 392.

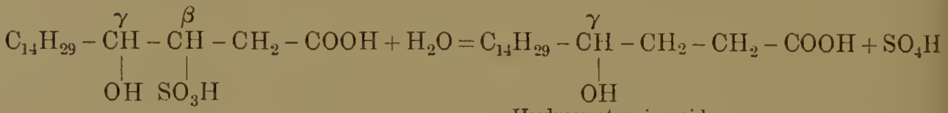
[3] The same reasoning holds good if the doubly-linked carbon atoms of oleic acid are in the ι and κ position.

As there is no reason why one acid should be formed in preference to the other, it may be assumed that both acids are formed in equal proportions. These acids are not very stable, and by merely allowing the crude product to stand, enough moisture is absorbed to produce a partial splitting up into SO_4H_2 and hydroxy acids, thus—

(1) 

$$C_{14}H_{29}-\overset{\gamma}{\underset{SO_3H}{CH}}-\overset{\beta}{\underset{OH}{CH}}-CH_2-COOH+H_2O=C_{14}H_{29}-CH_2-\overset{\beta}{\underset{OH}{CH}}-CH_2-COOH+SO_4H_2$$

β-Hydroxystearic acid.

(2) 

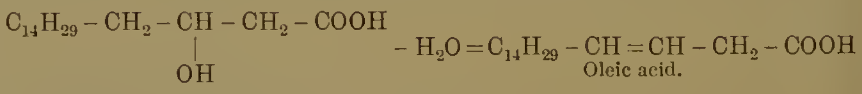
$$C_{14}H_{29}-\overset{\gamma}{\underset{OH}{CH}}-\overset{\beta}{\underset{SO_3H}{CH}}-CH_2-COOH+H_2O=C_{14}H_{29}-\overset{\gamma}{\underset{OH}{CH}}-CH_2-CH_2-COOH+SO_4H$$

γ-Hydroxystearic acid.

The latter acid — γ-hydroxystearic acid — immediately undergoes dehydration with formation of γ-stearolactone (p. 123).

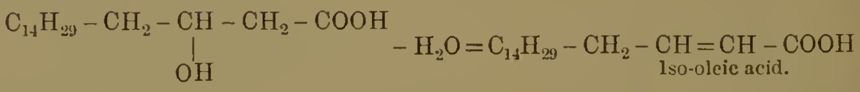
Another portion of the sulphostearic acid remains unchanged, but on boiling the crude mass with water the undecomposed portion is also converted into β-hydroxystearic acid and stearolactone, as shown.

In the subsequent distillation of the washed product the stearolactone already formed passes over unchanged, as also part of the β-hydroxystearic acid, whereas another portion is converted by dehydration into oleic *and* iso-oleic acids, thus—

(1) 

$$C_{14}H_{29}-CH_2-\underset{OH}{CH}-CH_2-COOH-H_2O=C_{14}H_{29}-CH=CH-CH_2-COOH$$

Oleic acid.

(2) 

$$C_{14}H_{29}-CH_2-\underset{OH}{CH}-CH_2-COOH-H_2O=C_{14}H_{29}-CH_2-CH=CH-COOH$$

Iso-oleic acid.

It is evident that unless distillation can be avoided, a complete conversion of oleic acid into solid products cannot be obtained.

In the "acid saponification" process the interaction takes place at a high temperature, and it is therefore readily intelligible that, since the chemical changes involved are reversible, a limit is reached beyond which the proportion of converted oleic acid cannot be increased.

With a view to ascertaining how far the conversion into saturated products takes place, *Lewkowitsch*[1] examined the action of sulphuric acid of varying strengths on oleic acid, both on a laboratory and on a large scale. The results are given in the following table:—

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[1] *Journ. Soc. Chem. Ind.* 1897, 392.

[TABLE

Action of Sulphuric Acid of Varying Strength at 5° *C. on Oleic Acid of Iodine Value* 80 (*Lewkowitsch*).

Oleic Acid.	Sulphuric Acid.		Iodine Value of the Product.
Molecules.	Containing SO_4H_2	Molecules.	
	Per cent.		
1	95	1	39·83
1	95	1	33·73
1	95	1	47·23
1	103 (fuming acid)	1	26·26
1	103 (fuming acid)	1	20·43
1	95	2	10·9
1	95	2	10·86
1	95	2	10·28
1	95	2	11·15
1	95	2	14·99
1	92	2	23·02
1	92	2	24·06
1	103 (fuming acid)	2	10·28
1	100·5 (mixture of fuming and concentrated acid)	2	14·40
1	100·5 (mixture of fuming and concentrated acid)	2	14·41
1	95	2·5	16·73
1	92·5	2·5	23·60
1	93	2·5	19·61
1	95	3	6·74
1	95	3	8·46
1	103 (fuming acid)	3	16·04

It will be seen that, contrary to expectation, the greatest amount of saturated products is not obtained when acid of 100 and more per cent SO_4H_2 is used. The crude products gave on examination the following results :—

Crude Product obtained by the Interaction of Sulphuric Acid and Oleic Acid at a Low Temperature (Lewkowitsch).

No.	Oleic Acid.	Sulphuric Acid.		Laboratory Experiments.			Works' Experiment.		
	Molecule.	Containing Per cent. SO_4H_2	Molecules.	Acid Value.	Saponification Value.	Iodine Value.	Acid Value.	Saponification Value.	Iodine Value.
1	1	95	1	157·8	179·2	31·8	98·4	198·3	24·8
2	1	100·5 (mixture of fuming and concentrated acid)	1	136·1	192·6	23·1	...	...	...
3	1	103 (fuming acid)	1	120·8	169·5	24·3	...	...	...

The crude product was distilled with superheated steam, and gave the numbers contained in the following table :—

Distillation of Crude Products with Superheated Steam (Lewkowitsch).

No.	Crude Product obtained from Oleic Acid and Sulphuric Acid containing—per cent. SO_4H_2.	Laboratory Experiments.						Works' Experiment.					
		First Fraction.	Second Fraction.	Third Fraction.	Fourth Fraction.	Residue.	Loss.	First Fraction.	Second Fraction.	Third Fraction.	Fourth Fraction.	Residue.	Loss.
		Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
	1 Mol. of oleic acid and 1 Mol. of SO_4H_2 :—												
1	95	27·4	42·7	20·4	1·9	4·0	3·6	30·0	30·0	26·5	...	6·2	7·3 [2]
2	100·5 (mixture of fuming and concentrated acid)	26·6	46·5	17·6	...	6·2	3·1	...	...	...	...	...	...
3	103 (fuming) . .	19·5	16·9	33·7	14·9	11·7	3·3	...	...	...	...	...	...
	1 Mol. of oleic acid and 2 Mols. of SO_4H_2 :—												
4	93	11·0	13·8	12·2	52·7	6·5	3·8	...	...	...	...	...	...
5	96·5	9·5	11·9	13·6	51·5	6·6	6·9 [1]	...	...	...	...	...	...

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[1] The still leaked a little.

[2] This high loss is due to the exceptional circumstances under which the experiment was carried out.

The several fractions obtained from the crude products, Nos. 1, 2, and 3, gave the numbers stated in the following tables :—

Characteristics of the several Fractions of Crude Product No. 1.

	Laboratory Experiment.				Works' Experiment.			Bulk.
	First Fraction.	Second Fraction.	Third Fraction.	Fourth Fraction.	First Fraction.	Second Fraction.	Third Fraction.	
Iodine value .	58	84·3	83·8	82·4	82·8	85·2	65·8	77·1
Neutralisation value	192	196·5	196·9	188·1	197·5	197·3	149·1	197·5
Saponification value	201	201·2	199·9	194·9	200·7	200·0	188·9	201·3
Melting point, ° C.	Liquid	27·2-28·3	27·2-29	25·5-29	20·2	25·3	24·9	23·45

Characteristics of the several Fractions of Crude Product No. 2.

	Laboratory Experiment.		
	First Fraction.	Second Fraction.	Third Fraction.
Iodine value . .	56·6	78·5	82·2
Neutralisation value .	197·6	198·2	194·6
Saponification value .	201·7	199·9	198·4
Melting point, ° C. .	Liquid	26·6-28·3	26·6-29

Characteristics of the several Fractions of Crude Product No. 3.

	Laboratory Experiment.			
	First Fraction.	Second Fraction.	Third Fraction.	Fourth Fraction.
Iodine value . .	61·9	73·4	81·4	84·1
Neutralisation value .	204·5	200·5	198·9	192·8
Saponification value .	209·1	203·3	199·7	194·5
Melting point, ° C. .	Liquid	Liquid	26·1-27·2	29-29·4

It should be borne in mind that the iodine numbers correspond to oleic + iso-oleic acid. The melting points of the products show that considerable quantities of iso-oleic acid have been formed. The small differences between the saponification and the neutralisation values prove that stearolactone is present in small quantities only.

David's[1] statement that 18-20 per cent of stearolactone are formed

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[1] *Journ. Soc. Chem. Ind.* 1897, 339.

in the cold by washing the product of interaction of oleic and sulphuric acids with an equal volume of water, removing the acid layer, dissolving the oily layer in an equal volume of water, and allowing to stand for twelve hours, has been shown by *Lewkowitsch*[1] to be erroneous, the separated crystals being practically β-hydroxystearic acid.

This has also been confirmed later on by *Shukoff*.[2]

Experiments made with a view to simulating the conditions obtaining in practice during the acid saponification process, by allowing sulphuric acid to interact with oleic acid at 132° C., and then distilling, are given in the following tables :—

Product obtained by the Interaction of Sulphuric Acid and Oleic Acid at 132° *C., and then distilled.* (*Works' Experiment.*) (*Lewkowitsch.*)

	Iodine Value.	Neutralisation Value.	Saponific Value.	Melting Point.
				° C.
Crude product	53·90	169·8	...	...
Bulk distillate from crude product	71·60	180·2	202·0	20·70
Bulk distillate :—				
Cold-pressed cake . . .	69·45	195·5	207·8	30·80
,, oil . . .	69·45	184·8	202·2	Liquid
Hot pressed cake . . .	72·10	202·8	206·7	43·05 (Titer test)

Product obtained by the Interaction of Sulphuric Acid and Oleic Acid at 132° *C. and then distilled.* (*Laboratory Experiment.*) (*Lewkowitsch.*)

	Yield.	Neutralisation Value.	Saponification Value.	Melting Point.
	Per cent.			° C.
First fraction .	10·8	181·16	201·3	Liquid
Second ,, .	39·0	167·38	193·9	25·5-30
Third ,, .	16·6	152·68	191·9	25·5-32
Residue . .	29·4	...	...	...
Loss . .	4·2	...	...	...

Although the proportion of stearolactone is higher than in the case of the crude products described in tables pages 1033 and 1034, still, the results set out in the last two tables prove that the interaction of sulphuric acid with oleic acid at higher temperatures cannot lead to a successful technical process.

Finally, I give the results of an experimental distillation of a crude product obtained by the interaction of one molecule of oleic acid and sulphuric acid of 95 per cent SO_4H_2, freed from hydroxystearic acid.

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[1] *Journ. Soc. Chem. Ind.* 1897, 390.

[2] French Patent, 328,604 ; German Patent, 150,798.

Distillation of Crude Product freed from Hydroxystearic Acid
(*Lewkowitsch*)

	Yield.		Melting Point.	
	I.	II.	I.	II.
	Per cent.	Per cent.		
First fraction .	24·0	23·4	Liquid	Liquid
Second ,, .	24·0	29·2	24-29	Oily
Third ,, .	{32·9}	{13·9}	24·4-29·4	24·4-27·7
Fourth ,, .	{7·8}	{22·9}	20·0-25·5	26·6-30·5
Residue . .	5·1	5·7	...	...
Loss . .	6·2	4·9	...	...

The considerable amount of liquid products obtained must not be looked upon as consisting entirely of unchanged oleic acid. These liquid substances consist to some extent of anhydrides, or polymerisation products.

Recently *Shukoff*[1] patented a method for converting oleic acid and its isomerides into lactones, by allowing about one molecule of concentrated sulphuric acid to act on one molecule of oleic acid at temperatures from 60°-90° C.

Hartl[2] recently patented a process for converting oleic acid into solid acids by treating *distilled* oleic acid with sulphuric acid. From the above given table of *Lewkowitsch* it is evident that this process merely represents a repetition of the above detailed experiments. *Hartl's* further suggestion to retain the hydroxystearic acid in the candle material by hydraulic expression has been anticipated in the above quoted paper by *Lewkowitsch*.[3]

The process of converting oleic acid into stearic acid by treatment with nickel powder in a current of hydrogen, based on *Sabatier* and *Senderen's* work, and patented by *Leprince* and *Siveke*,[4] has not yet been worked on a commercial scale.

(5) SAPONIFICATION BY MEANS OF TWITCHELL'S REAGENT

The reagent employed in this process is obtained by allowing an excess of sulphuric acid to act on a solution of oleic acid in aromatic hydrocarbons. The product obtained in case benzene is the aromatic hydrocarbon has been described by *Twitchell* as having the composition $C_6H_4(SO_3H)(C_{18}H_{35}O_2)$.[5]

The rationale of this process[6] is not yet fully understood. I explain the action of the reagent (Chap. ii. p. 45) by its power of emulsifying the glycerides. I have further given several tables

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[1] French Patent, 328,604.

[2] German Patent, 148,062.

[3] *Journ. Soc. Chem. Ind.* 1897, 390.

[4] German Patent, 141,029 ; cp. *Jahrbuch der Chemie*, xii. 370.

[5] *Journ. Amer. Chem. Soc.* 1899, 22.

[6] English Patent, 4741, 1898 ; German Patent, 114,491.

(pp. 46, 47) illustrating the action of several "Twitchell reagents" on oils and fats. Perhaps I may express the opinion that during the steaming sulphuric acid is generated as it were in *statu nascendi*, and thus acts on glycerides with the formation of sulpho-compounds, which are more readily hydrolysed by water than the glycerides themselves. The process differs, however, most essentially from the "acid saponification process," in that oleic acid is not converted into solid material; hence the fatty acids obtained by this process have the same composition as those yielded by the autoclave process.

The saponification proceeds best when the fatty matter contains a few per cent of free fatty acids at the outset. If these be present, 1½ to 2 per cent of the reagent are capable of hydrolysing glycerides. The process requires, however, a lengthy time for its completion, as is evidenced by the tables given, pp. 46, 47. The fatty acids are liable to become dark unless the access of air be excluded. Hence the fatty material obtained from this process is usually treated with concentrated sulphuric acid as described under processes Nos. 3 and 4, so that, strictly speaking, Twitchell's process would fall under the heading of the mixed process.

The foregoing processes yield as chief product solid candle material. By-products are oleic acid (see p. 1057), Glycerin (see p. 1084), and Stearine Pitch.

Stearine Pitch.—**Candle tar** (*Goudron*) is the residue left in the stills in the fatty acid distillation process. It is used for making oil gas; further, as a lubricant for heavy steel plate rollers—**hot neck grease**—and chiefly for caulking ships' decks. It is also used as an insulating material for cables. A specially suitable material for the last-named purpose is said to be obtained by heating the stearine pitch with sulphur at temperatures from 120°-175° C.[1]

Stearine pitch contains small quantities of free fatty acids and of neutral fat—together about 10 per cent—and chiefly hydrocarbons, due to destructive distillation. The definite acid and saponification values of stearine pitch permit of its being readily differentiated from petroleum residue (petroleum pitch).

The presence of neutral fat in stearine pitch differentiates it from the similar cotton stearine pitch and wool grease pitch (Chap. xvi.).

The candle material is made into finished candles by melting it and moulding in the well-known candle machines. These machines are of similar outer appearance as the machine shown in Fig. 83, except that the wick bobbins contained in the lower part of a candle moulding machine are absent.

According as the material is used in the manufacture of candles as such, or is admixed with other materials, we differentiate (*a*) stearine candles, or (*b*) mixed stearine and mineral wax candles.

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[1] Engl. Pat. 3045, 1894.

The once flourishing **tallow candle** industry has almost completely succumbed to the competition of the stearine and paraffin candle. The tallow dip candle has, therefore, but an insignificant local importance, although in the aggregate about 1000 tons are manufactured per annum in this country alone. Tallow candles are, as a rule, not adulterated. Their commercial examination is identical with that of tallow (p. 811).

Candles made from spermaceti (sperm candles) and from beeswax (wax candles) will be described p. 1055.

(*a*) Stearine Candles

The "stearine," "saponification stearine," "commercial stearic acid," obtained by the processes described under 1 and 2, consists practically of a mixture of stearic and palmitic acids.

The valuation of this material (as has been pointed out already incidentally) is based on its melting and solidifying points. The higher these are the more valuable is the material. A definite iodine value indicates the amount of oleic acid left in the press cakes; a definite difference between the neutralisation and the saponification values corresponds to neutral fat that has escaped hydrolysis, and has not been pressed out with the oleic acid.

For commercial purposes it is but rarely required to know the proportion of palmitic and stearic acids. If a direct determination of the stearic acid (p. 354) be inconvenient, the candle material may be valued, with sufficient accuracy for commercial purposes, on the basis of the numbers given in the table of solidifying points of mixtures of palmitic and stearic acids (p. 69), as also of the neutralisation value of the sample on referring to the table given on p. 408.

The "stearine" derived from the processes mentioned under Nos. (3) and (4), as also under (5), is also known as "commercial stearic acid." It is more correctly described as "distillation stearine." It is also valued by its melting and solidifying points. These are usually lower than those of the "saponification stearine." The iodine value of a "distillation stearine" furnishes a measure of the amount of iso-oleic acid present; and the difference between the neutralisation and saponification values is a measure of the amount of lactone present.

A complete analysis of "distillation stearine" would, therefore, embrace the determination of the iodine value, of the neutralisation and saponification values, and the direct determination of stearic acid; palmitic acid is then found by difference. By means of the iodine value it is possible to differentiate "saponification stearine" from "distillation stearine." The iodine value of the former rarely exceeds a few units, whereas "distillation stearine" gives iodine values varying, as a rule, between 15 and 30.

A considerable amount of neutral fat is contained in candle material intended for composite candles, consisting of a mixture of "stearine" and "cocoanut stearine." If an accurate determination of the neutral fat be desired, the safest plan is to saponify 50 grms. of the sample, and to determine the amount of glycerol.

Adulterants of genuine "stearine" are hydrocarbons (paraffin wax, ceresin), distilled grease stearine, and also carnaüba wax, which is sometimes admixed to increase the solidifying point of the candle material.

An indication of their presence is given by ascertaining whether any unsaponifiable matter is present. The examination of the isolated unsaponifiable matter is carried out by the methods given in Chapter IX. Thus paraffin wax and ceresin, as also carnaüba wax, can be detected. The presence of cholesterol points to admixture with "distilled grease stearine" (cp. p. 413, and also Chap. xvi.).

Candles consisting of "stearine" only are chiefly used in tropical or semi-tropical countries, since candles made from a mixture of stearine and paraffin wax bend and gutter owing to their low melting points.

In temperate climates candles are usually made from mixed material.

(*b*) Mixed "Stearine" and Mineral Wax Candles

(*a*) PARAFFIN WAX

Since a description of the manufacture of *paraffin wax* falls outside the scope of this work, a few notes only can be given. Paraffin wax is obtained from three sources, viz. petroleum, shale, and lignite.

Petroleum paraffin wax was, up to recently, chiefly obtained from North American petroleum. The proportion of paraffin wax in *American petroleum* varies from 2 to 4 per cent. Owing to the enormous amounts of petroleum raised in the United States very considerable quantities of paraffin wax have been obtained hitherto from this source. At present the output of North American petroleum is falling off. Most of the *Russian petroleums* contain inconsiderable quantities of paraffin wax; the Baku petroleum yields practically none, the Bibi-Eybat oil gives small quantities only. The petroleum from the Tcheleken Island forms, however, an exception; this oil yields about 5·5 per cent of wax.

The largest amounts of petroleum paraffin wax are at present obtained from *Rangoon petroleum*, which yields from 10 to 15 per cent of paraffin wax. The paraffin wax from the last-named source has the highest melting point of all paraffin waxes known hitherto. The *Assam oil* also yields considerable amounts of paraffin wax.

The *Roumanian* and *Galician petroleums* (with the exception of the Boryslaw petroleum) yield less paraffin wax than American petroleum. Petroleums from other sources, at any rate up till now, do not contribute to the production of paraffin wax.

The **lignite** worked up in the Saxo-Thuringian brown-coal tar industry yields a considerable quantity of paraffin wax, 10 to 15 per cent of which are recovered from the tar.

The **Scottish shale industry** forms at present one of the most important sources of paraffin wax. More than 20,000 tons of wax are produced annually from the shale. The wax is obtained by refrigerating the higher boiling fractions of the shale oil, and purifying the paraffin scale by the "sweating process." The yield of the wax varies with the quality of shale; from best crude shale tars as much as 15 per cent are obtainable.

The chemical composition of paraffin wax is not yet fully known, and varies with its origin. The American paraffin wax may be considered as consisting principally of a mixture of hydrocarbons of the ethane series C_nH_{2n+2}. The paraffin wax produced in the Saxo-Thuringian lignite tar industry contains a few per cent of olefines. Therefore the iodine values of paraffin waxes vary. Paraffin wax from petroleum must not be considered as identical with the wax obtained by destructive distillation. As a rule, the paraffin wax obtained by destructive distillation is superior in its technical application to petroleum paraffin wax.

The crude paraffin wax is termed in the trade "scale." This contains varying quantities of impurities or "dirt," water, and hydrocarbons of lower melting point, consisting chiefly of "soft paraffin." The latter, being valueless to the candle-maker, is termed "oil."

There is no sharp line of demarcation between the solid hydrocarbons and "oil"; as the hard paraffins pass gradually through "soft" or low melting point paraffins into "oil." The amount of "oil" pressed out in practical working depends naturally on various circumstances, such as temperature, pressure, length of time during which pressure is applied, etc., and it will thus be readily understood that a laboratory test for "oil" must be an arbitrary one.

Hence methods of testing are arranged by contract between buyer and seller and laid down in specifications.

The methods agreed upon by the *Scottish Mineral Oil Association* and certain *Representative Purchasers* for the sampling and testing of scale are the following:[1]—

Sampling of Scale.—The sample is taken by means of a metal tube, slightly conical, so that a cylindrical core of paraffin wax is obtained. Immediately after the sample has been drawn, it is thoroughly mixed, placed in suitable wide-mouthed bottles, which may be closed either with glass stoppers or good corks; if the latter are used, they should be covered with paraffin paper or soaked in melted paraffin wax before being inserted. The scale should be tightly packed and fill the bottles completely, as otherwise partial evaporation may occur, and moisture may condense in the upper portion. The bottles are then finally sealed in the usual manner.

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[1] *Journ. Soc. Chem. Ind.* 1891, 346.

Determination of Dirt in Scale.—The amount of dirt (fibres of press cloths, sand, etc.) in scale is determined by melting a weighed quantity—not less than 7000 grains (453·58 grms.)—and, after subsidence, pouring off the clear paraffin wax. The residue is then mixed with naphtha or petroleum ether, thrown on a weighed dry filter paper, washed with naphtha or petroleum ether, dried, and weighed.

Determination of Water in Scale.—The amount of water present in scale may be determined by either of the following processes, the determination by "subsidence"[1] having been abandoned as leading to erroneous results :—

(*a*) *Distillation from a Copper Flask.*—From 1 to 2 lbs. of the scale are heated in a copper flask connected with an ordinary Liebig condenser. The flask should be about 11″ high, 8″ in diameter at the bottom, and $1\frac{1}{4}''$ at the mouth. By means of a powerful Bunsen burner the water is volatilised and then condensed, a small quantity of light oil passing over at the same time. The distillate is received in a narrow graduated measure, so that the volume of water can be read off. As a little water usually adheres to the sides of the condenser tube, this must be washed off with petroleum ether or naphtha, previously saturated with water, and added to the bulk of water.

(*b*) *Price's Company's Method.*—500 grains (32·4 grms.) of the scale to be tested are weighed in a porcelain basin, and heated with constant stirring to 230° F. (110° C.), until bubbles cease to be given off; the loss is determined by weighing the residue.

500 grains (32·4 grms.) of the same scale, freed from water and dirt by melting at a gentle heat and by subsidence, are heated under exactly the same conditions (temperature, length of time) and the loss is determined. The loss now found is deducted from the loss ascertained previously; the difference is taken as the quantity of water present.

Determination of Oil in Scale.—A quantity of the scale, freed from water and dirt by melting and subsidence, is allowed to cool over night to a temperature of 60° F. (15·5° C.) The solid mass is then ground to powder, and a portion of this is used for the determination of oil.

250 grains (16·2 grms.) of the scale (or 150 grains (9·6 grms.) in the case of a scale containing much oil, say over 7 per cent) are then wrapped in fine linen press-cloth and a number of layers of filter paper, sufficient to absorb all the oil. The oil is then expressed in a press,[2] which must be provided with a pressure gauge.

The cup in which the scale is placed during the application of pressure must have an area of 20 square inches; the maximum pressure allowed is 10 cwts. per square inch, the working pressure being 9 cwts. per square inch. The scale must remain under pressure

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[1] Sutherland, *Journ. Soc. Chem. Ind.* 1887, 123.

[2] No one special form of press is recommended for general adoption. A description of several forms of press is given *Journ. Soc. Chem. Ind.* 1891, 346. Cp. also Carpenter and Leask, *Soap, Candles, etc.*, p. 324.

for fifteen minutes; the temperature of the scale and of the press should be 60° F.

Since the oil is determined in scale which has been freed from water and dirt, the result so obtained must be calculated on the original scale.

The finished material of the Scottish paraffin industry is sold as "soft" paraffin wax, if its solidifying point is below 48° C. = 118° F. Paraffin wax of a melting point above 120° F. is termed "hard" paraffin wax. The candle material produced in the Saxo-Thuringian industry has as a rule a melting point of 53°-56° C.; material of lower melting point (50°-52° C.) or higher melting point (60° C.) is but rarely produced.

Besides colour, transparency, and also odour, the most important criterion in the valuation of paraffin wax is the determination of the melting point. The specific gravity is of minor importance in the valuation of paraffin wax. Still, in controlling the process of manufacture the following tables will be found useful:—

Specific Gravity of Paraffin Waxes (Allen)[1]

No.	Origin of Sample.	Specific Gravity.		Solidifying Point.
		Solid, at 15° C.	Liquid, at 99° C.	°C.
1	Shale oil . . .	0·8666	0·7481	44·0
2	,, ,, . . .	0·8961	0·7494	47·0
3	,, ,, . . .	0·9000	0·7517	52·0
4	,, ,, . . .	0·9111	0·7572	58·5
5	American petroleum .	0·9083	0·7535	53·8
6	Ozokerit . . .	...	0·7531	61·5
7	Rangoon tar . .	0·8831	0·7571	49·0

Specific Gravities of Refined American Paraffin Waxes (I. I. Redwood)[2]

°F. at which the Gravity was determined.	Melting Point 108° F.	Melting Point 114° F.	Melting Point 120·5° F.	Melting Point 122·25° F.	Melting Point 122·75° F.	Melting Point 128·25° F.	Melting Point 133·25° F.
160	0·77069	0·77193	0·77391	0·77079	0·77023	0·77573	0·77723
155	0·77119	0·77330	0·77531	0·77149	0·77163	0·77653	0·77853
150	0·77309	0·77473	0·77657	0·77319	0·77283	0·77803	0·78003
145	0·77509	0·77620	0·77777	0·77519	0·77463	0·77973	0·78153
140	0·77679	0·77763	0·77847	0·77689	0·77633	0·78133	0·78333
135	0·77899	0·77953	0·78147	0·77869	0·77843	0·78303	...
130	0·78049	0·78113	0·78267	0·78029	0·77973	...	...
125	0·78199	0·78343	0·78441	...	...	...	...
120	0·78359	0·78473	...	...	...	...	...
115	0·78529	...	...	...	...	...	...

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[1] *Comm. Org. Anal.* vol. ii. p. 411.

[2] *Journ. Soc. Chem. Ind.* 1889, 163.

Specific Gravities of American Paraffin Waxes at 60° F. (I. I. Redwood)

Melting Point 106° F.	Melting Point 111·5° F.	Melting Point 120·5° F.	Melting Point 122·25° F.	Melting Point 125·75° F.	Melting Point 131° F.
0·87525	0·88230	0·89895	0·90105	0·90350	0·90865

The subjoined table, due to *Tervet*,[1] gives the melting points of each of twenty successive fractions into which three paraffin waxes of the melting points given below had been resolved. The temperatures are degrees Fahrenheit.

Melting Point of Fractions obtained from Paraffin Waxes

No. of Fraction.	Of Melting Point 126° F.	Of Melting Point 111° F.	Of Melting Point 102° F.
1	119·0	103·0	94·0
2	120·0	104·0	94·0
3	120·5	104·5	95·0
4	121·0	105·0	96·0
5	121·0	106·0	96·0
6	121·0	107·0	97·5
7	121·5	107·5	98·0
8	122·0	108·0	98·5
9	122·5	108·5	99·0
10	123·0	109·0	99·0
11	124·0	110·5	100·0
12	125·0	112·0	102·0
13	126·0	113·0	103·5
14	127·0	113·5	105·0
15	128·0	114·5	106·5
16	129·0	116·0	108·0
17	130·0	117·0	109·0
18	132·0	119·0	110·0
19	134·0	123·0	112·5
20	138·0	125·0	113·0

The melting and solidifying points of paraffin waxes almost coincide.

A uniform method of determining the solidifying point (or setting point) of paraffin wax has not yet been agreed upon. Hence in commercial analysis three different methods are in vogue, known as the "English test," the "American test," and the "German test" respectively.

English Test.—A test-tube, about 1 inch in diameter, is filled to the depth of about 2 inches with the melted paraffin, a small thermometer is inserted, and the mass stirred steadily, while the test-tube and its contents are allowed to cool slowly. The temperature

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[1] *Journ. Soc. Chem. Ind.* 1887, 356.

at which the thermometer remains stationary for a short time is the melting (setting) point. It should be noted that paraffin wax does not behave like mixed fatty acids, which on solidifying exhibit a sudden rise of temperature (p. 179). With paraffin wax the mercury column of the thermometer remains stationary at the melting point for about half a minute; but no rise takes place and the mercury then falls steadily.

American Method.—The melting point is determined as follows:—A sufficient quantity of wax is melted to fill three parts of a half-round dish, three and three-fourth inches in diameter. A thermometer with a round bulb is suspended in the melted mass so that the bulb is only three-fourths immersed. The melted paraffin is then allowed to cool slowly, and the temperature at which the first indication of "filming," extending from the sides of the vessel to the thermometer, occurs, is taken as the melting point.[1]

German method ("*Hallenser Vorschrift*").—A small beaker, 7 cm. high and 4 cm. in diameter, is filled with water and warmed to about 70° C. A small piece of the sample of paraffin wax is then thrown on the water so as to form, after melting, a disc of about 6 mm. diameter. A centigrade thermometer,[2] made according to the directions of the *Halle Association*, is then immersed in the water so that the bulb is entirely covered by water, and the mass allowed to cool slowly. The temperature at which a film is noticed on the paraffin wax is noted as the solidifying point.[3]

It is evident that the method of determining the solidifying point according to the American and German methods must lead to very uncertain results. The best plan would be to adopt the "English" method. With reference to the German method, it may be stated that the manufacturers of lignite paraffin wax are likely to adopt *Shukoff's* method (p. 180). *L. Weinstein*[4] has shown that the results obtained by the capillary tube method are very concordant.

In order to show that the melting and solidifying points of paraffin waxes differ, I append a few numbers ascertained in my laboratory:—

Paraffin Wax.	Melting Point. Capillary Tube.	Solidifying Point.
Rangoon	136·5° F. = 58·05° C.	135·75° F. = 57·65° C.
Scotch	132° F. = 55·5° C.	128° F. = 53·5° C.

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[1] Garrigues (*Journ. Soc. Chem. Ind.* 1895, 281) proposes to take this point by melting 30 to 50 grms. of the sample in a beaker, inserting the thermometer so that the bulb is completely immersed, and twirling the beaker continuously in one direction until the mercury ceases either to fall or rise. At first it falls rapidly and regularly, but then more steadily at the rate of 0·1° to 0·2° C. per minute after it has reached the highest point, at which it remains stationary for about half a minute. This highest point is taken as the melting point.

[2] This thermometer is supplied by Ferd. Dehne, or J. H. Schmidt, Halle a/S.

[3] *Journ. Soc. Chem. Ind.* 1887, 567.

[4] *Chem. Zeit.* 1887, 784.

Candles made exclusively from paraffin wax are too soft and bend too easily. Hence, in the manufacture of paraffin candles, "stearine" is usually admixed to an extent of from 5 to 15 per cent.

It has been pointed out already (p. 1039) that "stearine" is admixed with varying quantities of paraffin wax. The melting points of a mixture of paraffin wax and stearine cannot be calculated from the melting points of the components (cp. p. 69). It is therefore necessary for the proper control of the manufacture that each works' chemist construct an empirical table from the melting points of his special materials. Such empirical tables are given below for mixtures from (*a*) Scotch paraffin wax and "stearine," and (*b*) mixtures of Thuringian paraffin wax and "stearine."

Melting Points of Candle Material from "Mixed Paraffin Wax" (Scotch) and "Stearine" (I. I. Redwood)

A

Paraffin Wax.		Stearine.		Mixture.
Per cent.	Melting Point.	Per cent.	Melting Point.	Melting Point.
	°F.		°F.	°F.
90	102	10	121	100
80	,,	20	,,	98·5
70	,,	30	,,	100
60	,,	40	,,	104·5
50	,,	50	,,	110·5
40	,,	60	,,	111·0
30	,,	70	,,	113·5
20	,,	80	,,	117·5
10	,,	90	,,	119·0

B

Paraffin Wax.		Stearine.		Mixture.
Per cent.	Melting Point.	Per cent.	Melting Point.	Melting Point.
	°F.		°F.	°F.
90	120	10	123	118
80	,,	20	,,	116·50
70	,,	30	,,	114
60	,,	40	,,	112
50	,,	50	,,	110
40	,,	60	,,	109
30	,,	70	,,	113
20	,,	80	,,	118·50
10	,,	90	,,	119·50

C

Paraffin Wax.		Stearine.		Mixture.
Per cent.	Melting Point.	Per cent.	Melting Point.	Melting Point.
	°F.		°F.	°F.
90	120·25	10	129·75	118·50
80	,,	20	,,	116·75
70	,,	30	,,	114·50
60	,,	40	,,	112·25
50	,,	50	,,	113
40	,,	60	,,	118·75
30	,,	70	,,	122
20	,,	80	,,	124·50
10	,,	90	,,	127

D

Paraffin Wax.		Stearine.		Mixture.
Per cent.	Melting Point.	Per cent.	Melting Point.	Melting Point.
	°F.		°F.	°F.
90	125	10	121	123
80	,,	20	,,	121
70	,,	30	,,	119
60	,,	40	,,	117·50
50	,,	50	,,	114
40	,,	60	,,	111
30	,,	70	,,	107
20	,,	80	,,	114
10	,,	90	,,	117

E

Paraffin Wax.		Stearine.		Mixture.
Per cent.	Melting Point.	Per cent.	Melting Point.	Melting Point.
	°F.		°F.	°F.
90	130	10	121	128
80	,,	20	,,	125·50
70	,,	30	,,	123
60	,,	40	,,	121
50	,,	50	,,	118·50
40	,,	60	,,	114
30	,,	70	,,	109
20	,,	80	,,	115·50
10	,,	90	,,	118

F

Paraffin Wax.		Stearine.		Mixture.
Per cent.	Melting Point.	Per cent.	Melting Point.	Melting Point.
	°F.		°F.	°F.
90	132·50	10	129·75	130·50
80	,,	20	,,	128·50
70	,,	30	,,	126·50
60	,,	40	,,	124·25
50	,,	50	,,	121·0
40	,,	60	,,	117·75
30	,,	70	,,	119·50
20	,,	80	,,	125·25
10	,,	90	,,	127·50

[TABLE

Melting Points of Candle Material from "Mixed Paraffin Wax" (Thuringian) and "Stearine" (Scheithauer).[1]

Paraffin Wax. Per cent.	Of Melting Point. °C.	"Stearine" of Melting Point 54° C. Per cent.	Melting Point of Mixture. °C.
90·0	36·5	10·0	36·5
66·6	,,	33·3	39·0
33·3	,,	66·6	45·75
10·0	,,	90·0	51·75
90·0	37·5	10·0	36·5
66·6	,,	33·3	35·5
33·3	,,	66·6	47·0
10·0	,,	90·0	52·0
90·0	40·75	10·0	39·75
66·6	,,	33·3	40·50
33·3	,,	66·6	47·50
10·0	,,	90·0	52·0
90·0	45·0	10·0	44·0
66·6	,,	33·3	40·75
33·3	,,	66·6	48·0
10·0	,,	90·0	52·5
90·0	48·5	10·0	47·5
66·6	,,	33·3	45·0
33·3	,,	66·6	47·75
10·0	,,	90·0	52·50
90·0	50·0	10·0	49·0
66·6	,,	33·3	47·0
33·3	,,	66·6	47·5
10·0	,,	90·0	52·5
90·0	54·0	10·0	53·0
66·6	,,	33·3	49·0
33·3	,,	66·6	47·0
10·0	,,	90·0	52·5
90·0	56·5	10·0	55·5
66·6	,,	33·3	52·0
33·3	,,	66·6	47·5
10·0	,,	90·0	52·5

In the Thuringian industry five kinds of paraffin candles are produced at present: (1) Candles of the melting point 53°-54° C.

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[1] *Die Fabrikation der Mineraloele, Braunschweig.*

"*Adlerkerzen*"); (2) Candles of the melting point 54°-55° C. ("*Brillantkerzen*"); (3) Candles of the melting point 55°-56° C. ("*Kronenkerzen,*" "*Salonkerzen*"); (4) Candles of the melting point 56° C. ("*Baumkerzen*"); and (5) Candles made from 33·3 per cent stearine, and 66·7 per cent paraffin wax ("*Compositionskerzen*"). (*Höland.*[1])

The differentiation of paraffin waxes from different sources is a very difficult problem. A method may perhaps be based on the solubility in absolute alcohol.[2] The paraffin waxes from petroleum are comparatively easily soluble in absolute alcohol, whilst the Saxo-Thuringian waxes are soluble in this menstruum with greater difficulty. (Ceresin is almost insoluble.)

Holde records the following solubilities for a petroleum paraffin wax:[3]—

100 parts of absolute alcohol dissolve at 20° C. 0·1 -0·19 parts
100 ,, ,, ,, ,, 15° C. 0·015-0·017 ,,

whereas the Saxo-Thuringian paraffin waxes of melting point 55-56° C.[4] gave the following data:—

100 cc. of 99·5 per cent alcohol dissolve 0·031 grms. at 0° C.
100 cc. of 98·5 ,, ,, ,, 0·029 grms. at 0° C.

In the case of soft paraffin waxes (such as obtained in the Saxo-Thuringian industry) the solubility in alcohol increases with the decrease of the melting point.[5] The lower the melting point the greater is the loss by volatilisation at temperatures ranging from 100°-125° C. The following table given by *Eisenlohr* for soft Saxo-Thuringian paraffin waxes is instructive:—

Paraffin Wax of Melting Point.	Loss by Volatilisation	
	At 100° C.	At 125° C.
°C.	Per cent.	Per cent.
29·5	10·0	..
33·0	...	18·5
38·0	1·4	...
48·0	...	1·8

(β) CERESIN (OZOKERITE PARAFFIN)

The raw material used for the manufacture of ceresin is *ozokerite*, a natural bituminous product occurring in many parts of the globe in the vicinity of petroleum springs. The best known ozokerite is the

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[1] *Zeit. f. ang. Chem.* 1903, 614.

[2] Höland, *Zeit. f. ang. Chem.* 1903, 614.

[3] *Chem. Revue*, 1898, 114.

[4] Although the origin was not stated, the wax was most likely a Saxo-Thuringian wax, since these numbers given above have been confirmed by Eisenlohr, *Zeit. f. angew. Chem.* 1897, 334, for a lignite paraffin wax of the melting point 55·5° C.

[5] Eisenlohr, *Journ. Soc. Chem. Ind.* 1897, 701.

Galician ozokerite.[1] The ozokerite occurring on Tcheleken Island (the petroleum found there contains 5·5 per cent of paraffin wax, p. 1039) is much softer and darker than the Galician. Ozokerite is also found in Utah.[2]

The colour of crude ozokerite varies from a pure yellow to dark brown, depending on the admixed oxygenated resinous products. The degree of facility with which it can be kneaded between the fingers affords a rough test for valuing. The specific gravity varies from 0·91 to 0·97. The melting point depends on the proportion of liquid hydrocarbons contained in the ozokerite, it is therefore difficult to fix a lower limit for the melting point. The upper limit of about 100° C. is reached by the so-called "marble-wax."

The crude ozokerite is freed from water and mineral matter by a liquating process, and by boiling out with water. The ozokerite consists chiefly of hydrocarbons, but contains also oxygenated and wax-like bodies.

Impurities naturally occurring in ozokerite are water, liquid hydrocarbons, and clay. The longer ozokerite has been kept at a temperature above 70° C., and the more carefully the liquation process has been conducted, the purer will be the ceresin. Fraudulently added impurities are: asphaltum (mineral pitch), and residues from paraffin oil distilleries.

The examination of ozokerite consists in the determination of the loss on heating to 150° C. (this should not exceed 5 per cent), of its melting and solidifying points, and of the proportion of mineral matter. To estimate the latter small pieces are cut from the bottom of the blocks of ozokerite and exhausted with petroleum ether.

Ozokerite can, therefore, only be properly valued by closely following the process of refining adopted on the large scale.

Formerly ozokerite was distilled in a current of superheated steam with a view to converting it into white "paraffin wax." The yield from a good crude material varied from 60-70 per cent.

The behaviour with solvents of a "paraffin wax" thus obtained has been studied by *Pawlewski* and *Filemonewicz*.[3] The ozokerite paraffin had the specific gravity of 0·9170 at 20°, melted at 64°-65° C., and solidified at 61°-63° C.

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[1] Cp. J. Berlinerblau, *Das Erdwachs. Ozokerit und Ceresin*, 1897; J. Muck, *Der Erdwachsbergbau in Boryslaw*, 1903.

[2] Cp. E. B. Gosling, *School of Mines Quarterly*, 16, [1], 41.

[3] *Journ. Chem. Soc.* 1889; Abstr. 82.

[TABLE

Solvent.	Grms. of Ozokerite Wax dissolved by		Weight of Solvent required to dissolve completely 1 Part of Wax.
	100 grms.	100 c.c.	
Carbon bisulphide	12·99	...	7·6
Petroleum ether, boiling up to 75° C.; spec. grav. = 0·7233	11·73	8·48	8·5
Oil of turpentine; spec. grav. = 0·857, boiling point 158°-166° C.	6·06	5·21	16·1
Cumene, comm. boiling up to 160° C.; spec. grav. = 0·867	4·28	3·72	23·4
Cumene fraction, 150°-160° C.; spec. grav. = 0·847	3·99	3·39	25·0
Xylene, comm., b.p., 135°-143° C.; spec. grav. = 0·866	3·95	3·43	25·1
Xylene fract., 136°-138° C.; spec. grav. = 0·864	4·39	3·77	22·7
Toluene, comm., 108°-110° C.; spec. grav. = 0·866	3·83	3·34	26·1
Toluene fract., 108·5-109·5° C.; spec. grav. = 0·866	3·92	3·41	25·5
Chloroform	2·42	3·61	41·3
Benzene	1·99	1·75	50·3
Ethyl ether	1·95	...	50·8
Isobutyl alcohol, spec. grav. = 0·804	0·285	0·228	352·9
Acetone, 55·5°-56·5° C.; spec. grav. = 0·797	0·262	0·209	378·7
Ethyl acetate	0·238	...	419·0
Ethyl alcohol, 99·5° Tr.	0·219	...	453·6
Amyl alcohol, 127°-129° C.; spec. grav. = 0·813	0·202	0·164	495·3
Propionic acid	0·165	...	595·3
Propyl alcohol	0·141	...	709·4
Methyl alcohol, 65·5°-66·5° C.; spec. grav. = 0·798	0·071	0·056	1447·5
Methyl formate	0·060	...	1648·7
Glacial acetic acid	0·060	0·063	1668·6
Ethyl alcohol, 64·3° Tr.	0·046	...	2149·5
Acetic anhydride	0·025	...	3856·2
Formic acid (cryst.)	0·013	0·015	7689·2
Ethyl alcohol, 75° Tr.	0·0003	...	330000·0

At present ozokerite is exclusively worked up for the preparation of ceresin. For the valuation of ozokerite, *Lach*[1] recommends the following process:—

100 grms. of ozokerite are treated in a tared porcelain basin with 20 grms. of fuming sulphuric acid at a temperature of 170°-180° C. with constant stirring, until sulphur dioxide is no longer given off. After cooling, the dish is weighed and the loss taken as water and hydrocarbons. The mass is then again melted and 10 grms. of animal char, previously dried at 140° C., are stirred in. A tenth part of the mixture is then weighed off in a paper thimble, and extracted in a Soxhlet apparatus with petroleum ether, boiling below 80° C. The filter is dried at 130° C. and weighed; the loss gives the per-

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[1] *Journ. Soc. Chem. Ind.* 1885, 488.

centage of ceresin. The result may be checked by evaporating the petroleum ether solution and drying the residue at 180° C. The melting point of the isolated ceresin is then ascertained.

The proportion of fuming sulphuric acid may be varied, according as the colour of the refined product is desired to be yellow or white. *E. von Boyen*[1] states that even 5 grms. of ozokerite are sufficient for a satisfactory technical analysis.

The refined product is obtained on a large scale in the same manner as the analytical process indicates. It is termed **Ceresin** (French, *Cérésine;* German, *Ceresin, Erdwachs*), as it resembles beeswax in its physical characters; it is yellow, and can be made white and odourless by refining processes. It melts between 61° and 78° C.; the so-called "Sprungwachs" melts at 75° to 80° C.; its specific gravity is 0·918-0·922.

Ceresin is not suitable for candle-making as it smokes persistently; it is, however, used in the candle industry for stiffening the wicks of night-lights.

The most important test in the valuation of ceresin is the determination of the melting point. The various methods used in commercial analysis give different results, as exemplified by a sample of ceresin examined in my laboratory. The melting point by *Pohl's* method (p. 173) (which was stipulated in the contract) was 151°-157° F. In the capillary tube method (p. 175) the point of incipient fusion was 146° F., and the point of complete fusion 154° F. Tested by the "English method" (p. 1043) the melting point was 148°-150° F. It is therefore necessary to lay down in contracts the method by which the sample should be tested.

The method proposed by *Finkener*[2] to determine the dropping point of ceresin for Custom House purposes, with a view to distinguishing ceresin from mixtures of ceresin and paraffin wax, has been criticised by *Holde*,[3] who showed that mixtures of ceresin and paraffin wax can be prepared having dropping points considerably higher than 66° C., the lowest limit laid down for pure ceresin by *Finkener*. Moreover, mixtures of pure ceresin and carnaüba wax may "drop" at a point which lies far above that temperature, and the presence of paraffin wax in the mixture can be easily masked by adding carnaüba wax. This method cannot, therefore, be recommended.

Owing to the high price of ceresin it is very extensively adulterated with paraffin wax and bleached rosin. In order to raise the melting point carnaüba wax is added. Rosin is detected by a definite acid value of the sample. Carnaüba wax is detected in the unsaponifiable matter by the method described, p. 377.

Commercial ceresin is frequently coloured with turmeric and other colouring matters. On shaking the melted sample with alcohol the colouring matters pass into the alcoholic solution.

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[1] *Zeit f. angew. Chem.* 1898, 383.

[2] *Mitth. Königl. Techn. Versuchsanstalten*, 1899, vii. 100.

[3] *Ibid.* p. 103. Cp. Bindewald, *Chem. Zeit.* 1903, 433.

Since *paraffin wax* is much more readily soluble in absolute alcohol than ceresin, which is almost insoluble in this menstruum, paraffin wax may be detected in ceresin by heating the sample with absolute alcohol, allowing to cool, and placing a few drops of the alcoholic solution on an object glass, when the residue will appear crystalline under the microscope.

The following table, due to *Berlinerblau*, may furnish some additional means of ascertaining the purity of a given sample :—

Ceresin. Per cent.	Paraffin Wax. Per cent.	Melting Point. °C.	Solidifying Point. °C.	Specific Gravity at		
				15° C.	83°-85° C.	95° C.
100	0	70-73	69·5	0·921	0·7835	0·774
95	5	69-73	68·5	0·919		
90	10	68-72	66·5	0·9175	0·7800	
80	20	66-71·5	65·0	0·914	0·7775	
70	30	64·5-70	63·0	0·910	0·7750	
60	40	62-69	62·0	0·907		
50	50	58·5-67	60·0	0·904	0·7705	
40	60	56·5-65	59·0	0·900		
30	70	54·5-62	57·0	0·897		
20	80	52·5-58·5	54·0	0·894		
10	90	49·5-54·5	49·0	0·892		
0	100	47-52	47·0	0·889	0·7655	0·756

Graefe[1] has shown that admixtures of ceresin—from 1 per cent to 10 per cent—with paraffin wax cannot be detected by the determination of the solidifying point, since mixtures of a paraffin wax of the solidifying point 54·8° C. with 1 to 10 per cent of ceresin gave the same solidifying point of 54·8° C.

The detection of small quantities of ceresin in paraffin wax is carried out by *Graefe* in the following manner :—

One gram of the sample is dissolved at 20° C. in 10 c.c. of carbon bisulphide. In case more than 10 per cent of ceresin be present no clear solution is obtained at 20° C. If the solution has remained clear, 1 c.c. is shaken in a test-tube with a mixture consisting of 5 c.c. of ether and 5 c.c. of 96 per cent alcohol, and kept at 20° C. In case the sample consists of pure paraffin wax (Saxo-Thuringian) of a melting point up to 54° C., no separation takes place; if, however, ceresin be present, flocks separate, simulating somewhat the appearance of alumina precipitated from a very dilute solution by ammonia. *Graefe* states that even 1 per cent of ceresin can thus be detected.

In the case of paraffin wax of a higher melting point than 54° C., the method breaks down, as such wax gives a precipitate with the ether-alcohol mixture, although of a different appearance from that obtained in the presence of ceresin. *Sommer*[2] objects to this method on the ground that only American and Saxo-Thuringian

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[1] *Chem. Zeit.* 1903, 248.

[2] *Ibid.* 1903, 298.

paraffin waxes behave as described above, whilst Scotch, Galician, and the high melting "Java" paraffin waxes might be taken on the strength of the above test to represent a mixture of paraffin wax and ceresin.

Graefe,[1] however, maintains the correctness of his method.

(γ) MONTANWAX

German—*Montanwachs*

Montanwax has been prepared by *E. von Boyen* [2] by extracting the bitumen from dried Thuringian lignite by means of volatile solvents. The bitumen, freed from the solvent, yields on being distilled with superheated steam under ordinary pressure a white hard mass melting above 70° C., and consisting of a mixture of fatty acids and a hydrocarbon. The acid, named "montanic acid," melts at 80° C., and has the specific gravity 0·915. The hydrocarbon is a saturated compound of the specific gravity 0·920, and crystallises from benzene in shining white laminæ, melting at 60·5° C. By heating with concentrated sulphuric acid the hydrocarbon is carbonised (difference from paraffin wax).

This hydrocarbon appears to be a product of decomposition, for on distilling the extracted bitumen with superheated steam *in vacuo* the then resulting product consists of montanic acid and of an alcohol. This would point to the bitumen being a true wax (in the chemical sense). The wax is hydrolysed by superheated steam, and its components distil over in the uncombined state. The alcohol is separated from the acid by hot pressing.

A sample of "montanwax" examined in my laboratory gave the following characteristics:—

Melting point	80° C.
Neutralisation value	123·01
Unsaponifiable in neutralised mass	6·40 per cent
Saponification value	126·58
Unsaponifiable in saponified mass	3·58 per cent

According to *Hell*,[3] montanic acid [4] has the formula $C_{29}H_{58}O_2$, and melts at 84° C. On calculating the neutralisation and saponification numbers found in my laboratory to $C_{29}H_{58}O_2$, the following would appear to be the composition of montanwax:—

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[1] *Chem. Zeit.* 1903, 408.

[2] D. R. P. 101,373, 116,453, *Zeit. f. angew. Chem.* 1899, 64; 1901, 1110.

[3] *Zeit. f. angew. Chem.* 1900, 556.

[4] "Geoceric acid" (Kraemer and Spilker, *Berichte*, 1902, 1217).

	From Neutralisation Value.	From Saponification Value.
	Per cent.	Per cent.
Acid	96·04	98·82
Unsaponifiable . . .	6·40	3·58
	102·44	102·40

From these numbers the conclusion may be drawn that the product still contains some undecomposed "wax." The excess of over 2 per cent requires, however, further explanation. This material has been proposed by the inventor as a candle material; no information has, however, been published hitherto as to its suitability for this purpose.

Smaller importance attaches to the manufacture of candles from spermaceti and from beeswax.

(*c*) Sperm Candles

Sperm candles are made from refined spermaceti (p. 903); they are at present still used as an illuminant, but have been almost completely replaced by the cheaper stearine and paraffin candles. Up till recently sperm candles have been employed as the standard for photometrical measurements by gas examiners in this country, and are still in use.

Spermaceti alone cannot be employed for candles, the material being too brittle; beeswax, tallow, stearine, paraffin wax, and ceresin are therefore admixed with it. These admixtures are detected by the methods described (p. 905).

The rules for the preparation of standard sperm candles for photometrical purposes, published by the Metropolitan Gas Referees,[1] prescribe that for the purpose of rendering spermaceti less brittle, best air-bleached beeswax, melting at or about 144° F. (62° C.), shall be used (and no other material), and that the proportion of beeswax to spermaceti shall be not less than 3 per cent, nor more than 4·5 per cent. The spermaceti itself shall be so refined as to have a melting point lying between 112° F. and 115° F. (45°-46° C.) The melting point is to be determined as follows:—

"A small portion of the spermaceti is melted by being placed in a short test-tube, the lower end of which is then plunged in hot water. A glass tube drawn out at one end into a capillary tube about 1 mm. in diameter is dipped, narrow end downwards, into the liquid sperma-

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[1] *Journ. Soc. Chem. Ind.* 1894, 65.

ceti, so that when the tube is withdrawn 2 or 3 mm. of its length are filled with spermaceti, which immediately solidifies. The corresponding part of the exterior of the tube is also coated with spermaceti, which must be removed. The narrow part of the tube is then immersed in a large vessel of water of a temperature not exceeding 100° F. (37·8° C.). The lower end of the tube, which contains the spermaceti, should be three or four inches below the surface, and close to the bulb of a thermometer. The upper end of the tube must be above the surface, and the interior of the tube must contain no water. The water is then slowly heated, being at the same time briskly stirred, so that the temperature of the whole mass is as uniform as possible. When the plug of spermaceti in the tube melts it will be forced up the tube by the pressure of the water. The temperature at the moment when this movement is observed is the melting point."

(*d*) Beeswax Candles

Beeswax candles are not moulded like the candles described hitherto, as they adhere strongly to the moulds of the candle machines, and even if they can be made to leave them, they lose their shape, or crack. The tapers and thicker cables of beeswax are made by "drawing," *i.e.* pulling a wick by means of simple machinery through the melted wax, and then through a die until it has acquired the desired thickness. Large wax candles are made by "pouring" melted beeswax on to a wick hanging vertically from a hoop. When the layer has cooled, a fresh layer of wax is poured on to it until the candle has reached the desired thickness. Finally, the candles are rolled on a marble slab under a board until they assume the desired length. Beeswax candles, therefore, show concentric layers, which can be easily peeled off, if necessary, for separate examination.

White beeswax intended for candle-making can only be bleached by air; chemically bleached wax is unsuitable, for not only does the texture ("grain") become coarse and crystalline, but also the burning power of the wax is inferior.

The examination of the raw material is carried out in an identical manner to that described under the examination of beeswax; the reader must, therefore, be referred to pages 890-903. It may, however, be added that beeswax intended for candle-making is not adulterated with Japan wax, myrtle wax, and carnaüba wax, as these ingredients render a beeswax candle practically useless. Hence candles which contain carnaüba wax are free from beeswax proper. Thus a candle, represented to be a beeswax candle, gave on analysis the following results:—

Carnaüba wax	60 per cent.
"Stearine"	25 ,,
Ceresin	15 ,,

An estimate made by the writer as to the annual production of candles in this country leads to 45,600 tons, which may be distributed over the different materials as follows :—

Tallow	1,000 tons.
Stearine	2,190 ,,
Paraffin Wax	42,200 ,,
Ceresin	100 ,,
Spermaceti	50 ,,
Beeswax	60 ,,
	45,600 tons

2. OLEIC ACID, OLEINE, ELAÏNE, COMMERCIAL OLEIC ACID

The commercial oleic acid is a by-product of the candle industry; and, as has been pointed out already, is obtained in two qualities —"saponification oleine" and "distillation oleine."

The saponification oleine is usually of dark colour, and unless carefully freed from "stearine" by refrigeration, contains considerable quantities of solid fatty acids. Hence, the iodine value of such oleine lies much below 90 (cp. p. 103). All the neutral fat which has escaped hydrolysis in the autoclave processes is found in this oleic acid. Hence, its saponification value will be higher than its neutralisation value.

All the unsaponifiable matter contained in the fats subjected to autoclaving is likewise found in the oleine.

The "distillation oleine" obtained by the sulphuric acid saponification process or by the "mixed process" is a distilled product, and hence represents a pale transparent oil. It usually contains small quantities of solid fatty acids, so that the iodine value of properly manufactured "distillation oleine" from tallow lies between 80 and 86.

Before the process of distilling fatty acids had reached its present state of perfection, large quantities of hydrocarbons (cp. p. 1019) distilled over together with the oleine, owing to destructive distillation of neutral fat taking place in the still. It was then possible to distinguish "distillation oleine" from "saponification oleine" by the presence of hydrocarbons in the former. At present, however, the manufacturing processes are carried out in such a manner that the distillation oleines of commerce are practically free from products of decomposition. The following table contains a few analyses of typical "oleines" as obtained in the saponification of neutral fats :—

[TABLE

Commercial Oleine from	Consistence.	Colour.	Specific Gravity at 15·5° C.	Free Fatty Acids.	Unsaponifiable.	Neutral Fat.		Iodine Value.	Observer.
						Direct.	By Difference.		
				Per cent.	Per cent.	Per cent.	Per cent.		
Tallow by autoclave process	Clear liquid	Pale brown	0·8996	96·3	1·3	...	2·5	...	Allen
,, ,, ,,	Fluid, with slight deposit	Brown	0·9055	80·3	2·2	...	17·5	...	,,
,, ,, ,,	,, ,, ,,	Dark brown	...	88·2	...	11·5	...	...	Lewkowitsch
Tallow and palm oil (Belgian)	Clear liquid	Dark brown	...	86·6	...	14·0	...	...	,,
,, (?) ,,	,, ,,	Pale brown	...	93·8	3·9	...	2·3	...	Allen
,, (?) ,,	Semi-solid	Brown	0·9085	83·7	2·9	13·4	17·0	...	,,
Autoclave oleine ,,	,,	Pale brown	0·9014	96·2	4·8	...	...	...	,,
,, ,, French .	Contained much solid	Pale brown	0·8987	84·5	10·3	3·3	2·0	...	,,
Tallow by lime saponification	...	...	...	89·4	2·0	...	8·6	...	,,
Tallow and palm oil by acid saponification . . .	Clear liquid	Pale brown	...	92·2	3·2	...	5·6	..	Lewkowitsch
Tallow and palm oil by acid saponification . . .	Solid at 15° C.	White	...	97·8	1·0	...	1·2	...	,,
Tallow and palm oil by lime saponification . . .	Clear liquid	Pale brown	...	94·6	2·6	3·4	...	...	,,
Tallow by autoclave process	,, ,,	,,	...	...	...	...	...	80	,,

Other oleines obtained from waste products of the fat industries, and containing large proportions of unsaponifiable matter, have been described already under the headings: "Wool Oils" (Table, p. 954), and "Distilled Oleines from Recovered Grease" (p. 959). An exhaustive examination of "oleine" of the latter kind has been given by way of example in Chapter XI. p. 413 (cp. also Chap. XVI.).

Another kind of oleine is obtained from "Cotton Seed Foots" (Chap. XVI.).

If the oleine be intended for the manufacture of soap the unsaponifiable matter only need be determined, a certain proportion of solid fatty acids or of neutral fat being rather desirable than otherwise. For rapid valuation of oleine, intended for soap-making, it is sufficient to saponify with alcoholic potash, and divide the saponification value found into 200 × 100,[1] when the percentage of saponifiable fat is obtained with sufficient accuracy.

If it be required to ascertain whether a sample of oleine has been obtained from tallow only, or from a mixture of tallow with a vegetable fat, the phytosteryl acetate test (p. 371) will give the readiest answer.

"Distilled grease oleine" in best "distillation oleine" is detected by means of the cholesterol and isocholesterol reactions, as also by the presence of a notable percentage of unsaponifiable matter. The metallic salts of oleic acid have been described p. 107. (Cp. also "Metallic Soaps," p. 1083.)

II. SOAP MANUFACTURE

Chemically speaking, soaps are the salts of the fatty acids. Hence, as explained in Chapter III., we must discern between salts of the alkali metals and salts of the alkaline earths and heavy metals.

In technical parlance, however, the term soap is usually applied to the alkali salts of the non-volatile fatty acids. According as the base be soda or potash, we differentiate between *hard soaps*, *soda soaps*, and *soft soaps*, *potash soaps*.

1. HARD SOAPS, SODA SOAPS

The earliest processes of manufacturing hard soap consisted in boiling oils and fats with causticised wood ashes, the potassium carbonate contained therein being converted into caustic potash by boiling with lime. The potash soaps so obtained were converted into soda soaps by treating the soap paste repeatedly with common salt. The theory underlying this manufacturing process has been fully explained in Chapter III. p. 84. This process has not yet completely died out, and is still being used on a small scale in those localities where a cheap and plentiful supply of wood ashes is

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[1] Taking 200 as the saponification value of oleic acid.

obtainable. The manufacture of soap in these localities is still passing through the stage of evolution from a house industry to a manufacturing process.

Later on the wood ashes were replaced by "soda ashes" obtained by burning sea-weeds ("barilla," "kelp"). The manufacture of sodium carbonate by the Leblanc process almost completely extinguished the use of barilla and kelp, and the soap-maker is thus enabled to obtain manufactured soda (soda ash, sodium carbonate) which he causticises himself in the same manner as the wood ashes were causticised. Thus the caustic soda required for the saponification of oils and fats was manufactured in the soap works themselves, and is to a very large extent still being produced by the soap manufacturer.

The development of modern chemical industry led to the production of solid caustic soda in the alkali works, so that the soap-maker has at present the choice of either buying the caustic soda in the solid form or himself manufacturing his caustic soda solution ("caustic lyes") from soda ash, by causticising sodium carbonate, and subsequently concentrating the dilute caustic soda solution in vacuum evaporators of simple or multiple type, such as are shown in figures Nos. 85-88 (pp. 1090-1093).

On a manufacturing scale two processes for the production of hard soaps from oils and fats are in use, viz. (1) soap-making by the cold process; (2) soap-making by the boiling process.

(1) Soap-making by the Cold Process

The most suitable oils and fats for the manufacture of soaps by the cold process are the oils belonging to the cocoa nut oil group (Chap. XIV. p. 738), these oils having the property of being convertible into soaps on being stirred together with concentrated caustic soda solutions of about the specific gravity 1·35. The plant required for this manufacture is of the simplest construction, and merely consists of an iron or wooden frame into which the fat, previously brought to a temperature of about 35° C., is placed; it is then stirred whilst an accurately measured quantity of caustic soda of sp. gr. 1·35 is run in. The frame is then covered and allowed to stand, when the mass develops some heat, sufficient to complete the process of saponification within twenty-four hours.

The simplicity of this process naturally led to the market being flooded with "cold" soaps, prepared by unskilled operators, so that these soaps usually contained a considerable excess of caustic soda. The prejudice which has arisen against this class of soap in consequence of faulty manufacture is, however, unfounded, as it is not difficult to prepare practically neutral soaps by careful working. The quantity of caustic soda required for saponification must be calculated from the saponification value of the fatty material. The fifth column of the Table on page 1063 will be found useful for practical purposes.

The ready saponification which the oils of the cocoa nut oil group undergo in the cold enables the soap-maker to incorporate with the cocoa nut oils other oils and fats which by themselves cannot be saponified completely by strong caustic soda in the cold, the heat which is spontaneously developed facilitating the saponification of those oils and fats which are not readily saponifiable by strong caustic alkalis. It is therefore evident that the greater the proportion of less readily saponifiable (by strong alkalis) oils and fats (*e.g.* olive oil, tallow, lard), the higher must be the initial temperature at which the oils and fats are intermixed with the strong caustic soda lye.

The soaps so obtained naturally contain the whole amount of glycerol that results from their saponification.

Castor oil also has the property of forming a soap under the same conditions as the oils belonging to the cocoa nut oil group.

Since 100 parts of neutral glycerides yield practically 150 parts of finished soda soap, it is possible to theoretically calculate the composition of a soap made by the "cold process." Thus a soap made from an oil of the cocoa nut oil group having the saponification value 240, and the mean molecular weight of the mixed fatty acids 200, will have the following composition:—

	Per cent.
Fatty anhydrides	54·50
Na_2O	8·86
Glycerol and water	36·64
	100·00

The quantities of soap made by this process are comparatively small; the bulk of the commercial soaps being made by the "boiling process."

(2) SOAP-MAKING BY THE BOILING PROCESS

In the boiling processes either natural oils and fats or the fatty acids derived therefrom are used.

a. Soap-making by Boiling Natural Oils and Fats with Caustic Soda

The process of making soaps by boiling the glycerides with caustic soda solutions is used on a most extensive scale, and is practically the only one which yields soaps of uniformly good quality, colour, and hardness. In this process the oils and fats are introduced into a cylindrical vessel—soap kettle, soap copper, soap pan,—and churned up by means of steam, when a dilute caustic soda solution is run in, which assists the emulsifying of the fat and induces hydrolysis. The theory of the process has been described on page 53, and it need only be pointed out that it is necessary to commence saponifying with a dilute solution, as the employment of strong caustic soda in the case of most oils and fats—with the exception of the oils belonging to the cocoa nut oil group and of castor oil—"cuts" the soap-paste as do salt solutions (page 82). As has been shown on page 53, an excess of caustic soda is required to complete the saponification. After completion of the saponification the mass in the soap pan consists of a mixture of soda salts of the fatty acids with water, in which the glycerol formed in the course of hydrolysis and the excess of caustic soda are dissolved. In order to convert the soap-paste into commercial soap, it is necessary to separate the soda salts from the excess of caustic soda, and from the water by adding salt (page 82), whereby the soda salts are thrown up and the mass is separated into two layers:—a lower aqueous layer consisting of a solution of salt, glycerol, and excess of caustic soda, and an upper layer representing a curdy mass of soap containing about 30-35 per cent of water. The lower layer is drawn off, and worked up for the recovery of the glycerol (p. 1087).

The curdy soap remaining in the pan is boiled up with water ("closed"), so as to form a homogeneous paste, which is again boiled with a little caustic soda to ensure complete saponification, and separated in the manner described above.

The soap may again be treated in the same manner, to remove impurities which impair its colour, and is at last "fitted," *i.e.* brought into the condition of finished soap.

The art of the soap-maker consists in so "fitting" the soap that it contains just the proper amount of water, which may be called the water of constitution, and still be "open" enough to allow the intermingled heavier aqueous solution, as also the impurities, which consist to a notable extent of iron salts of fatty acids, to settle out. After the mass has been allowed to settle for a few days, there is found at the bottom of the soap pan a small amount of alkaline solution, above which rests a layer of dark soap, intermixed with the salt solution and the excess of caustic soda, the dark colour being chiefly due to metallic soaps. This layer is termed in practice "nigre" (*i.e.* black, a term taken over from the Marseilles soap-makers). Above this rests the bulk of the finished soap, "neat soap," covered on the top by a thin layer of solidified soap of a spongy condition, owing to the occlusion of the air which has gradually risen during the settling process to the top of the mass.

The excess of caustic alkali in the "neat" soap should be very small; its amount depends on the care used during the manufacture.

Up till recently soap-making was considered an art, the details of which were supposed to depend on valuable secrets which were only in the possession of the practical soap-maker. Hence the "fitting" was left to him, and the amount of caustic soda used in the process depended entirely on his judgment. It must, however, be acknowledged that through constant practice, and in consequence of the more stringent demands of the public as regards quality of soap, soap-making has reached a considerable degree of perfection, so that the production of practically neutral soaps has become very general.

From the treatise on hydrolysis of soap (Chap. III.) rules can be derived as to how the process of soap-boiling should be conducted so as to effect saponification with the least excess of caustic soda. With this object in view it is necessary to work with caustic lyes of known strength. Tables containing the percentages of caustic soda, derived from the specific gravities of solutions prepared from pure caustic soda, are given in Tables 67 and 68 of my *Laboratory Companion*, page 109. The following two tables will be found useful in controlling the consumption of caustic soda in soap-works.

Caustic Soda Solutions required to saponify Fats of Mean Molecular Weight 670 *(Cocoa nut Oil, Palm kernel Oil)*

Weight of Fat in Tons.	Gallons of Solution.			
	20° Twaddell = S. G. 1·1.	40° Twaddell = S. G. 1·2.	60° Twaddell = S. G. 1·3.	71° Twaddell = S. G. 1·355.
	NaOH.	NaOH.	NaOH.	NaOH.
·05	21·01	9·46	5·72	4·59
·1	42·02	18·92	11·43	9·18
·15	63·03	28·38	17·15	13·76
·2	84·04	37·84	22·86	18·35
·25	105·05	47·30	28·58	22·94
·3	126·06	56·76	34·29	27·53
·35	147·07	66·22	40·01	32·11
·4	168·07	75·68	45·72	36·70
·45	189·08	85·14	51·44	41·29
·5	210·09	94·60	57·15	45·88
·55	231·10	104·06	62·87	50·46
·6	252·11	113·52	68·58	55·05
·65	273·12	122·98	74·30	59·64
·7	294·13	132·44	80·01	64·23
·75	315·14	141·91	85·73	68·81
·8	336·15	151·37	91·44	73·40
·85	357·16	160·83	97·16	77·99
·9	378·17	170·29	102·87	82·58
·95	399·18	179·75	108·59	87·16
1·0	420·19	189·21	114·30	91·75
2·0	840·37	378·41	228·60	183·50
3·0	1260·56	567·62	342·90	275·26
4·0	1680·74	756·83	457·20	367·01
5·0	2100·93	946·04	571·50	458·76
6·0	2521·12	1135·24	685·80	550·51
7·0	2941·30	1324·45	800·10	642·26
8·0	3361·49	1513·66	914·40	734·02
9·0	3781·67	1702·86	1028·70	825·77
10·0	4201·86	1892·07	1143·00	917·52

[TABLE

Caustic Solutions required to saponify Fats of Mean Molecular Weight 860 (*Tallow, Cottonseed Oil, Olive Oil, etc.*)

Weight of Fat in Tons.	Gallons of Solution.			
	20° Twaddell = S. G. 1·1.	40° Twaddell = S. G. 1·2.	60° Twaddell = S. G. 1·3.	71° Twaddell = S. G. 1·355.
	NaOH.	NaOH.	NaOH.	NaOH.
·05	16·37	7·37	4·45	3·57
·1	32·74	14·74	8·90	7·15
·15	49·10	22·11	13·36	10·72
·2	65·47	29·48	17·81	14·30
·25	81·84	36·85	22·26	17·87
·3	98·21	44·22	26·71	21·44
·35	114·57	51·59	31·17	25·02
·4	130·94	58·96	35·62	28·59
·45	147·31	66·33	40·07	32·17
·5	163·68	73·70	44·52	35·74
·55	180·04	81·07	48·98	39·31
·6	196·41	88·44	53·43	42·89
·65	212·78	95·81	57·88	46·46
·7	229·15	103·18	62·33	50·04
·75	245·52	110·55	66·79	53·61
·8	261·88	117·92	71·24	57·18
·85	278·25	125·29	75·69	60·76
·9	294·62	132·66	80·14	64·33
·95	310·99	140·03	84·60	67·91
1·0	327·35	147·41	89·05	71·48
2·0	654·71	294·81	178·10	142·96
3·0	982·06	442·22	267·14	214·44
4·0	1309·42	589·62	356·19	285·92
5·0	1636·77	737·03	445·24	357·41
6·0	1964·12	884·43	534·29	428·89
7·0	2291·48	1031·84	623·34	500·37
8·0	2618·83	1179·24	712·38	571·85
9·0	2946·19	1326·65	801·43	643·33
10·0	3273·54	1474·05	890·48	714·81

The finished "neat" soap, whilst still warm, is run into soap frames, holding from 12 to 15 cwts. of soap, and allowed to cool therein. Such neat soap is termed "curd soap" or "genuine soap." Lower classes of soaps are manufactured by mixing with the "neat" soap, in mixing machines, or in the frames themselves, various solutions of salts as required by the quality of the desired soap.

Simultaneously perfumes and colouring matters are incorporated with the soap.

The soap in the frames requires a few days to solidify. The sides of the soap-frames are then removed, and thus a rectangular soap block is left. This block is cut at first into slabs of the required thickness, either by hand or in a slabbing machine shown in Fig. 81.

These slabs are placed into a barring and tabletting machine, such as shown in Fig. 82.

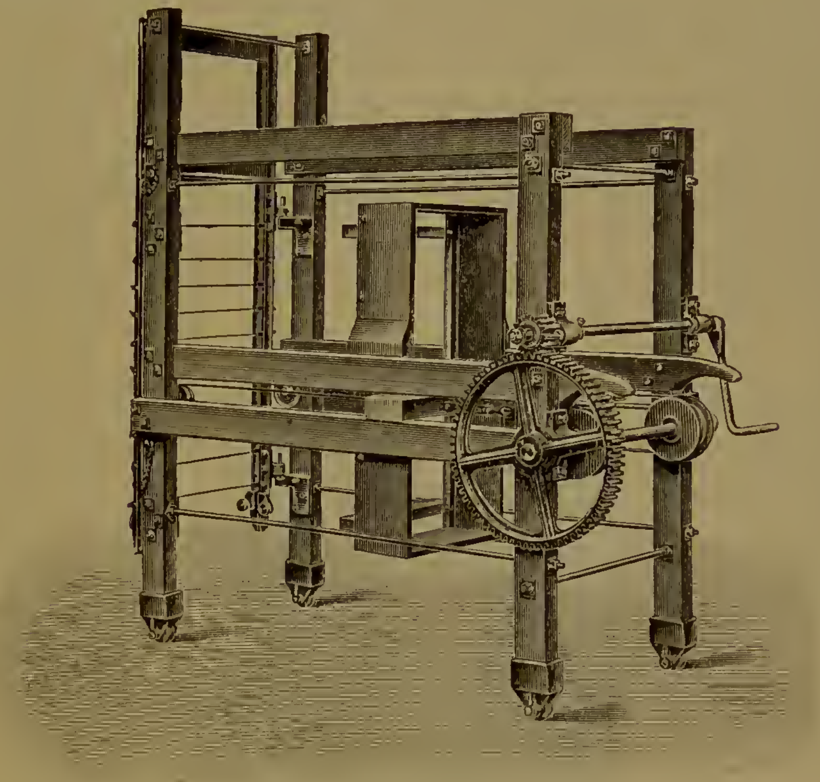

Fig. 81.

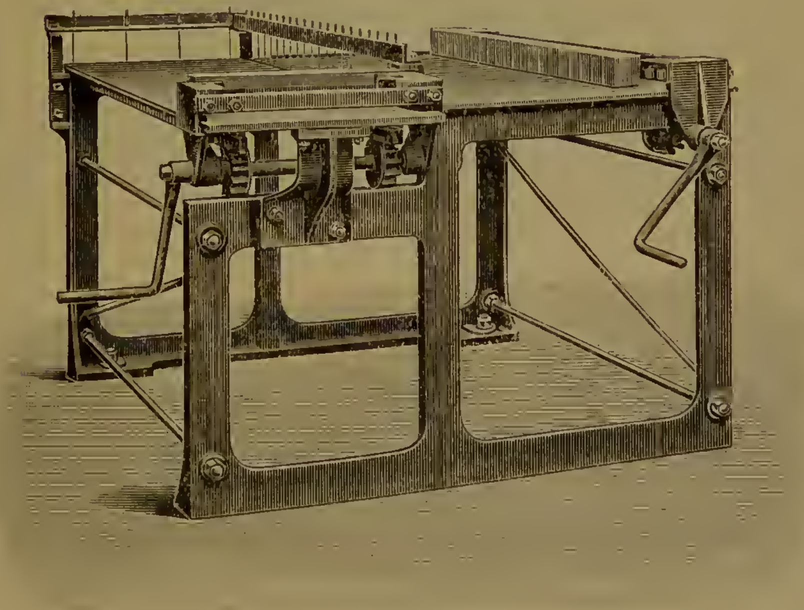

Fig. 82.

The slabs are put into the recess on the right-hand side of the figure, and by turning the handle pushed through a number of wires, so that they emerge on the other side in the form of bars, usually weighing 3 lbs. By working the handle shown on the left-hand side of Fig. 82 the bars are pushed against the wires shown at the end, and thus finally obtained in the form of the familiar soap cake.

The stamping of the soap cakes is a mere mechanical process.

The process of solidification of the soap being a somewhat lengthy one, attempts have not been wanting to shorten the time required from the finishing operation in the soap pan to the conversion of the solidified soap into the marketable bar or cake.

The writer attempted to effect this by sending the soap through a long worm, cooled artificially,[1] but the soap so obtained represented an unsaleable mass, owing to the crystalline structure of the soap having been destroyed. Another attempt to effect the rapid solidification of the hot soap mass was made by moulding the soap in the same manner as candles are moulded.[2] The machine used for this purpose (Fig. 83) is fashioned after the well-known candle-moulding machine, and was chiefly intended for the manufacture of toilet soaps, in which the crystalline structure, which is so much valued in household soap, is destroyed. The hot soap mass was run into the several moulds shown in the figure, and after suitable cooling, the solidified soap was expelled in the same manner as moulded candles are forced out.

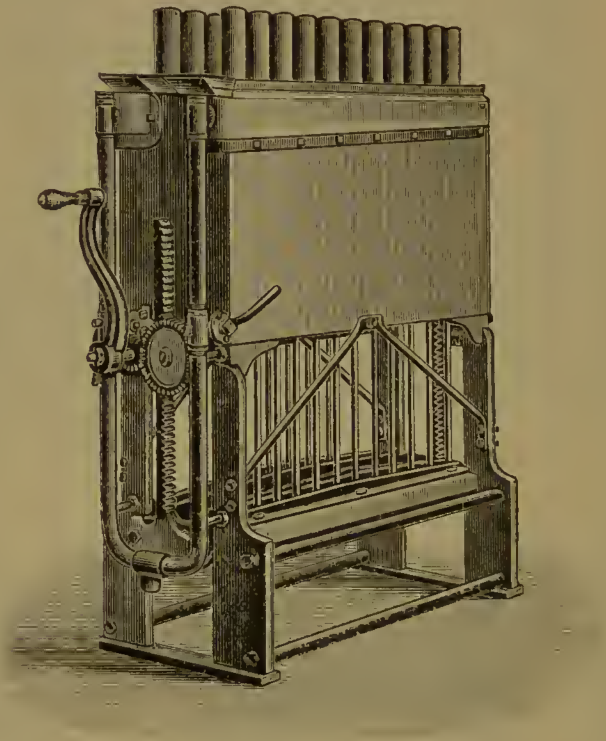

Fig. 83.

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[1] Lewkowitsch, *Problems in the Fat Industry*, 1903, 597.

[2] English Patent, No. 4581, 1893.

This machine proved unsuitable for household soaps, but the idea underlying the construction of this machine has been recently taken up and patented by *Schnetzer*.[1] At present nothing can be said as to the success obtained by his plant. Another attempt to shorten the time required for solidification has been made by *Klumpp*,[2] whose press is best described as being modelled after a copying press, the sides of which are completely closed. The hot soap is run into the press, and when full the soap is cooled rapidly and compressed, so that the soap bars are ready for dividing into tablets immediately. A combination of the principles embodied in these two methods may be said to be contained in *Schrauth's* patent.[3]

100 parts of neutral glycerides of the mean molecular weight 860 yield practically 150 parts of finished soaps. The mean molecular weight of the fatty acids of such glycerides is 275. An easy calculation will show that 100 parts of fat require 10·81 parts of Na_2O; hence the finished soap contains 7·21 per cent of Na_2O [150 : 10·81 : : 100 : x], with which are combined 61·8 per cent of fatty anhydrides [31 : 266 : : 7·21 : x], corresponding to 63·9 per cent of fatty acids [266 : 275 : : 61·8 : x].

The percentage composition of a "genuine soap" is therefore—

	Per cent.
Fatty anhydrides	61·80
Sodium Oxide, Na_2O	7·21
Water	30·99
	100·00

Pure commercial soda soaps made by the processes described contain practically the proportion of water given above; this might be called their water of constitution, inasmuch as a soap cannot be made in the soap kettle with less water.

β. Soap-making by Boiling Fatty Acids with Alkali

Soap being a soda salt of fatty acids, it is evident that soap can also be prepared by neutralising fatty acids by means of caustic soda, and working and fitting the resulting soda soap as described above. Since fatty acids are capable of expelling carbonic acid from sodium carbonate when boiled in aqueous solution, soap can also be prepared by boiling fatty acids with sodium carbonate. Such processes have been in practical use ever since the stearine candle industry was established, as the manufacture of oleic acid soap afforded a natural outlet for the by-product.

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[1] English Patent, No. 18,932, 140; German Patent, 140,505; 144,108; 145,079.

[2] German Patent, 140,846.

[3] German Patent, 144,805.

FATTY ACIDS MADE BY THE AUTOCLAVE PROCESS

The higher the pressure at which the autoclaves were worked, the more discoloured became the fatty acids, and the darker were therefore the soaps made from autoclaved material. Hence soaps so prepared did not find favour with the public, and were therefore chiefly used for "milling" purposes.

The increased demand for glycerin that has arisen during the last three decades, and which led to the recovery of the glycerin from the soap lyes (p. 1087), has again drawn attention to soapmaking from fatty acids, by decomposing first the neutral fats into glycerol and fatty acids, with a view to recovering a purer glycerin than is obtained in the "salt crude," and then converting the fatty acids into soap, by boiling with caustic soda or sodium carbonate, or a mixture of both.

Fatty material autoclaved at a pressure of 15 atmospheres is, of course, too dark to be converted into saleable soap. Even material autoclaved at a pressure of 8 atmospheres leads to an off-coloured product. Therefore a compromise was proposed between the process of the candlemaker and the proper process of the soapmaker, as described under *a*, by hydrolysing the fats with the assistance of bases (cp. p. 1007) in an autoclave at a somewhat lower pressure—usually 5 to 6 atmospheres—so as to prevent, as far as possible, discolouration of the fatty material. From a glance at the table given on p. 1011 it will be seen that the bulk of fat is hydrolysed in an autoclave during the first few hours; hence, by reducing both the pressure under which the autoclave is worked and the length of time at which the autoclaved material is kept under pressure, the discolouration can to some extent be diminished. It has further been attempted to reduce the discolouration by introducing zinc oxide and zinc dust into the autoclave, but these palliatives have not led to satisfactory results. From the theoretical explanation given in Chapter II., it is evident that the hydrolysis (saponification) cannot be a complete one. Indeed, in all the different autoclaved materials intended for soapmaking that I have examined during recent years, the percentage of unsaponified fat varied from 10 to 20 per cent.

This autoclaved material may be converted into soap by the "boiling process" with a mixture of sodium carbonate and caustic soda, since sodium carbonate is not capable of saponifying the neutral fats at the ordinary pressure (see p. 60).

This process has several serious drawbacks as compared with the ordinary process described under *a*. In the first instance, the glycerol corresponding to the amount of unsaponified fat is lost, as it would not pay to recover it. But over and above that, it has been shown by extensive practical experience that soaps prepared from such material are softer and of lower grade as regards colour when contrasted with the soaps made by the "boiling process" from the corresponding neutral oils and fats. The saving in the difference of cost of caustic alkali as against the equivalent amount of sodium carbonate by no means counterbalances the losses incurred through the above explained disadvantages. Hence this process of manufacturing soap is practically not used in this country. On the Continent, where the demands of the public are less rigorous, this process has gained some ground, especially in those small establishments where the recovery of glycerin from soap lyes is thought to be too cumbersome. But even there it is not denied that soaps made from autoclaved material cannot compare in quality with those manufactured from natural oils and fats by the boiling process.

FATTY ACIDS MADE BY TWITCHELL'S PROCESS

The fatty acids made by this process are practically free from neutral fats, and therefore require less caustic soda in addition to sodium carbonate than those made by autoclaving. It has been pointed out already that the fatty acids, unless very carefully protected from the access of air, become discoloured, which of course affects the colour of the finished soap unfavourably. The soaps which have been submitted hitherto to the writer are not comparable in colour with those made by the "boiling process."

FATTY ACIDS PREPARED BY THE FERMENT PROCESS

The theoretical explanation of this process has been given on pp. 47 to 51. This process [1] is now being tried on a manufacturing scale, but hitherto sufficient data have not been published to allow definite conclusions to be derived therefrom. The writer suggested last year [2] the isolation of the ferment, as the ground castor seed leads to a troublesome middle layer. This suggestion is contained in a patent by *Nicloux*,[3] who proposes to triturate castor seed with castor oil and centrifuge the mass, whereby a separation of the practically inactive aleuron grains from a more active mass is obtained.

The preparation of fat-splitting enzymes and their possible application to industrial purposes is now being systematically investigated by *Fokin*.[4] It may be added that an enzyme has been isolated [5] from the seeds of the Para rubber tree (p. 493), which is stated to have a very high fat-splitting power.

2. SOFT SOAP—POTASH SOAP

Potassium hydrate is the base used preponderantly in the manufacture of soft soap, small quantities only, if any, of caustic soda

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[1] English Patent, 22,111, 1902 ; German Patent, 145,413.

[2] Lewkowitsch, "Problems in the Fats Industry," *Journ. Soc. Chem. Ind.* 1903, 596.

[3] French Patent, 335,902 ; cp. also Hoyer, *Berichte*, 1904, 1436.

[4] *Chem. Revue*, 1904, 48, 69, 118.

[5] In the Imperial Institute.

being employed. The resulting potash soap retains all the glycerol formed during the process of saponification. The manufacture of potash soap is much simpler than that of hard soaps, since it consists in practically only one operation, viz. in "boiling" the glycerides with caustic alkali solutions in a pan, no salting out being required. Hence the resulting product, after being properly "fitted," can be run straightway from the boiling-pan into the vessels in which the soap is sold. If it be desired to "fill" the soap with salt solutions, this is done in the soap pan after the saponification is completed.

The following two tables, giving the amounts required theoretically for the saponification of glycerides, may be found useful in practice (cp. p. 1063):—

Caustic Potash Solutions required to saponify Fats of Mean Molecular Weight 670 (*Cocoanut Oil, Palm Kernel Oil*).

Weight of Fat in Tons.	Gallons of Solution.			
	20° Twaddell = S. G. 1·1.	40° Twaddell = S. G. 1·2.	60° Twaddell = S. G. 1·3.	71° Twaddell = S. G. 1·355.
	KOH.	KOH.	KOH.	KOH.
·05	21·31	10·42	6·97	5·80
·1	42·63	20·84	13·95	11·60
·15	63·94	31·26	20·92	17·40
·2	85·25	41·68	27·90	23·21
·25	106·57	52·10	34·87	29·01
·3	127·88	62·52	41·85	34·81
·35	149·19	72·94	48·82	40·61
·4	170·51	83·36	55·79	46·41
·45	191·82	93·78	62·77	52·21
·5	213·13	104·20	69·74	58·01
·55	234·45	114·62	76·72	63·81
·6	255·76	125·04	83·69	69·62
·65	277·07	135·46	90·67	75·42
·7	298·39	145·88	97·64	81·22
·75	319·70	156·30	104·61	87·02
·8	341·01	166·72	111·59	92·82
·85	362·33	177·14	118·56	92·62
·9	383·64	187·56	125·54	104·42
·95	404·95	197·98	132·51	110·22
1·0	426·27	208·40	139·49	116·03
2·0	852·54	416·80	278·97	232·05
3·0	1278·80	625·19	418·46	348·08
4·0	1705·07	833·59	557·94	464·10
5·0	2131·34	1041·99	697·43	580·13
6·0	2557·61	1250·39	836·92	696·16
7·0	2983·88	1458·79	976·40	812·18
8·0	3410·14	1667·18	1115·89	928·21
9·0	3836·41	1875·58	1255·37	1044·23
10·0	4262·68	2083·98	1394·86	1160·26

Caustic Potash Solutions required to saponify Fats of Mean Molecular Weight 860 (*Tallow, Cottonseed Oil, Olive Oil, etc.*).

Weight of Fat in Tons.	Gallons of Solution.			
	20° Twaddell = S. G. 1·1.	40° Twaddell = S. G. 1·2.	60·0 = Twaddell = S. G. 1·3.	71° Twaddell = S. G. 1·355.
	KOH.	KOH.	KOH.	KOH.
·05	16·60	8·12	5·43	4·52
·1	33·21	16·24	10·87	9·04
·15	49·81	24·35	16·30	13·56
·2	66·42	32·47	21·73	18·08
·25	83·02	40·59	27·17	22·60
·3	99·63	48·71	32·60	27·12
·35	116·23	56·82	38·03	31·64
·4	132·84	64·94	43·47	36·16
·45	149·44	73·06	48·90	40·68
·5	166·05	81·18	54·33	45·20
·55	182·65	89·30	59·77	49·72
·6	199·26	97·41	65·20	54·24
·65	215·86	105·53	70·63	58·75
·7	232·47	113·65	76·07	63·27
·75	249·07	121·77	81·50	67·79
·8	265·67	129·88	86·94	72·31
·85	282·28	138·00	92·37	76·83
·9	298·88	146·12	97·80	81·35
·95	315·49	154·24	103·24	85·87
1·0	332·09	162·36	108·67	90·39
2·0	664·19	324·71	217·34	180·78
3·0	996·28	487·07	326·01	271·18
4·0	1328·37	649·42	434·68	361·57
5·0	1660·47	811·78	543·35	451·96
6·0	1992·56	974·14	652·01	542·35
7·0	2324·65	1136·49	760·68	632·74
8·0	2656·74	1298·85	869·35	732·14
9·0	2988·84	1461·20	987·02	813·53
10·0	3320·93	1623·56	1086·69	903·92

Potash soaps, if manufactured with sufficient care, can be made to be devoid of free alkali. As a rule, however, commercial potash soaps contain an excess of caustic alkali, as also potassium carbonate, which is usually added to impart to the soap the proper consistence. If impure caustic potash be used, all the impurities, notably sulphates, carbonates, chlorides, etc., will be found in the finished soap.

Potash soaps contain much larger quantities of water than hard soaps. Genuine soft soaps made in the pan retain so much water that 100 parts of neutral glycerides yield 240 parts of commercial potash soap.

From these data the theoretical composition of a genuine soft soap can be calculated.

Suppose a fat of the mean molecular weight 860 has been saponified. Its saponification value is about 195, or, in other words, it requires 19·5 per cent of KOH = 16·42 per cent of K_2O for saponification.

The 240 parts of potash soap obtained from 100 parts of such fat contain, of course, 16·42 parts of K_2O; therefore we have in the soap 6·843 per cent of K_2O [240 : 16·42 : : 100 : *x*].

As the mean molecular weight of the fatty acids is about 275, the corresponding amount of the fatty anhydrides is 275 – 9 = 266. Since 47·1 parts of K_2O combine with 266 parts of fatty anhydrides, we have in the soap 38·7 per cent of fatty anhydrides [47·1 : 266 : : 6·843 : *x*]. The remainder, ignoring any carbonate and excess of caustic alkali, consists of glycerol and water.

The composition of a genuine potash soap should, therefore, theoretically, be—

	Per cent.
Fatty anhydrides	38·700
Potassium oxide, K_2O	6·843
Glycerol and water	54·457
	100·000

In the same manner as soda soaps can be made from fatty acids, also potash soaps can be obtained from fatty acids. Regarding the quality of soaps so made, the same strictures apply that have been detailed above, p. 1068.

Special kinds of soaps are **milled soaps (toilet soaps), transparent soaps,** and **soap powders (dry powders, washing powders).**

Milled Soaps (Toilet Soaps).—These soaps are prepared from "genuine" soaps made by the "boiling process," containing, as explained above, about 30 per cent of water. As a preparatory process the bulk of the water must be removed. This is done by cutting the soaps into fine shavings by means of a rotatory cutting machine, and spreading the shavings on trays in a steam-heated drying chamber. In large establishments the shavings are carried on an endless band through a drying apparatus. The soaps thereby lose about 20 per cent of water, and are then ready to be worked in a milling machine (or crushing machine), between granite rollers, into fine shreds. At this stage of the operation, colouring matters and perfumes, as also medicaments, are intermixed. The mass is repeatedly passed between the rollers until a complete intermixture is obtained. The shredded soap is then transferred into a machine in which the shreds are compressed by means of a screw and driven against a plate perforated with a number of small holes, so that the soap passes this part of the machine in the form of single thick threads, which are again compressed at a somewhat elevated temperature, so that the threads coalesce and leave the machine in the shape of a continuous bar of soap.

Transparent Soaps.—Genuine transparent soaps are prepared by dissolving genuine soap in alcohol, distilling off the excess of alcohol, and moulding the gelatinous residue; the soap thereby solidifies to a transparent cake. With this class of soaps there must not be confounded the cheap transparent soaps made by "filling" soaps, derived in part from castor oil, with sugar solutions.

Soap powders, dry soaps, washing powders are prepared by grinding together hard soaps with sodium carbonate. The hard mass obtained thereby is broken up in a mill, and then reduced to fine powder in a disintegrator. These soaps are valued on the basis of the real soap they contain. Frequently inert matter, such as sodium sulphate, kieselguhr, etc., are incorporated with the soap.

The number of substances that are admittedly incorporated with soaps in order to impart to them some valuable properties, real or supposed, is almost legion. It must be left to the analyst to decide in each individual case whether petroleum, paraffin wax, tar oils, sulphur, etc., are to be classed amongst adulterants or not.

In the present condition of the soap trade, and in view of the demands made by public taste, it is difficult to say what constitutes adulteration.

Rosin is a legitimate substitute of fatty matter, the sodium salts of the rosin acids possessing valuable detergent properties. Hence any rosin acid present in the fatty matter which is obtained on decomposing the soap with mineral acid is looked upon as so much fatty acid, and is therefore included in the fatty acids. If a separate determination of the rosin acids be required, Twitchell's method (p. 394) should be employed.

Sodium silicate and **borate** also possess detergent properties, but these substances must be considered as standing on the border-line between legitimate constituents and adulterants.

Colouring matters in soaps cannot be considered as illegitimate admixtures, as coloured soaps are demanded in commerce. Therefore, provided the colouring matter be harmless, no objection can be raised. The analyst will, at most, only be required to state whether certain colouring matters contain poisonous metals or not.

Ethereal oils in soaps have almost become a necessary ingredient, even as regards better class household soaps. Their quantity will naturally be very small, and need not, as a rule, occupy the attention of the analyst.

There can, however, be no doubt that adulteration has taken place in case "fillers" or "weighting substances" have been found in soaps. Starch, clay, talcum, etc. fall under this category. Sand in a soap sold as a "sand soap" must, of course, not be considered a fraudulently added material.

In the following lines I describe the most reliable methods (leaving out a number of proposed processes) applicable in the examination and valuation of commercial soaps. No attempt is made to indicate a complete course of analysis embracing the search for all substances that may possibly be present, as such a course would be of little practical use.

Sampling of the Soap

Great care must be exercised in sampling in order to avoid serious errors in the determination of water. On exposure to the air, soap dries on the surface, and once a "skin" is formed the outer portions of a cake protect to some extent the inner portions from losing water by evaporation. In the case of hard soap the sample for analysis should therefore be taken from the centre of the cake by cutting away all the outer portions; to what extent this must be done will be gathered in most cases by inspecting the sample, a transverse section showing to what depth drying has taken place. Such devices as taking a sample by means of a cork-borer, or by cutting a transverse slice from the cake in order to obtain an "average" sample, lead to erroneous results. If the sample under examination be a fresh made soap (containing about 30 per cent of water) a fairly large portion should be weighed off rapidly, as the soap is apt to give up perceptible quantities of moisture to the dry atmosphere of the balance case. For the same reason the sample should not be sliced before weighing, except perhaps in case a milled toilet soap or dried soap be under examination.

In these cases the well-known contrivances for preventing loss of moisture during weighing must be resorted to.

Similar precautions must be taken in the case of soft soap. If a keg of potash soap has to be sampled, the soap must be taken from the centre.

(*a*) *Determination of Fatty Matter and of Total Alkali.*

A rapid, and for the purposes of commercial analysis, sufficiently accurate process is the following:—

Weigh off accurately 5 to 10 grms. of the sample (or 50 grms., on a balance sensitive to centigrammes), and dissolve in hot water in a beaker or porcelain basin by heating gently; stir continually with a glass-rod so as to prevent the soap from caking on to the bottom of the vessel. Add a few drops of methylorange, and run in gradually hydrochloric, or dilute sulphuric acid (or dilute nitric acid if chlorides and sulphates are to be determined), until there is an excess of mineral acid. Heat with constant stirring, until the separated fatty acids have melted into oily drops, add about 5 grms. (or 20 grms. for 50 grms. of soap) of dry beeswax, or paraffin wax,[1] weighed accurately on a tared watch-glass (which is used afterwards for weighing the fatty matter), and heat again until the mixture of fatty acids and wax has collected on the top of the liquid as a clear, transparent oily layer free from specks. Rinse off the glass rod with boiling water, heat until the fatty matter has again collected into one mass, remove the vessel from the source of heat, and allow to solidify by cooling. A

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[1] The addition of wax may, of course, be omitted if it is known that the fatty matter will set to a solid cake on cooling.

white precipitate on the bottom of the beaker will indicate the presence of silicate or "fillings" insoluble in mineral acids.

The solidified cake is then detached from the vessel by means of a platinum spatula, lifted out of the liquid, rinsed off with cold water, and placed on filter paper. Any small quantity of fatty substance adhering to the sides of the vessel is carefully scraped off and added to the cake. Dry the cake with filter paper, place it on the watch-glass used before, bottom side upwards, allow to dry in a desiccator, and weigh. (For the control of works' operations, when 50 grms. should be used, it is sufficiently accurate to weigh immediately after drying with filter paper, taking care that no moisture remain in the cavities of the cake.) Should the cake contain any cavities (which only occurs when the fatty matter has not been heated properly), enclosing water and perhaps even acid, the cake may be remelted in a basin over water, taken off and dried as described before.

From the weight thus found the weight of the wax is deducted, and the difference returned as **fatty matter.** If no closer examination is made, this is as a rule returned as **fatty acids.** This is, however, only correct if the absence of *neutral fat*, *wax*, and *unsaponifiable matter* has been proved, *rosin acids* being looked upon as so much fatty acids, unless determined separately.

In case the soap contains foreign matter (such as fibre, etc.), from which the fatty matter does not separate readily, it is best to extract the fatty acids with ether, and determine their weight after evaporating off the ether. In some cases the soap can be separated from the foreign matter, by dissolving in alcohol and filtering off.

Any *soluble* fatty acids which are present in the soap pass to some extent into the acid liquid; as a rule, they may be altogether neglected, except where cocoa nut and palm nut oil soaps are examined. In that case it is best to work with concentrated solutions, or, if convenient, to add common salt, which throws out the bulk of the soluble acids, so that the remainder may be mostly disregarded. If great accuracy be required the soap is decomposed under ether, and the fatty acids thus transferred into the ethereal solution. A less accurate method is to titrate with standard alkali until the aqueous solution is neutral to methylorange, then to add phenolphthalein and again titrate with decinormal alkali. The alkali used in the second titration may be calculated to, say, caprylic acid, $C_8H_{16}O_2$, molec. weight 144, and the amount so found added to the bulk of the fatty acids.

A very large number of processes have been recommended by various chemists purporting to introduce greater accuracy, but in my opinion they unnecessarily complicate the analysis, without offering any advantages.

If by subsequent examination the soap has been found free from neutral fat, wax, and unsaponifiable matter (p. 1079), the fatty matter is returned as **fatty acids.** If a complete analysis of the soap is desired they are calculated to fatty anhydrides. Since 100 parts of stearic acid, $C_{18}H_{36}O_2$, correspond to 96·83 parts of stearic anhydride

$(C_{18}H_{35}O)_2O$, and similarly 100 parts of palmitic acid, $C_{16}H_{32}O_2$, to 96·48 parts of palmitic anhydride, $(C_{16}H_{31}O)_2O$, and 100 parts of oleic acid, $C_{18}H_{34}O_2$, to 96·81 parts of oleic anhydride, $(C_{18}H_{33}O)_2O$, no appreciable error is committed if 3·25 per cent are deducted, or, what amounts to the same, if the percentage of fatty acids be multiplied by 0·9675. With regard to rosin acids, cp. p. 392.

The more fatty acids a sample contains the more actual soap is present. A comparison of the result of the analysis with the theoretical composition of soaps given above will assist in the valuation of the soap. Any hard soap containing more than 64 per cent of fatty acids has either dried spontaneously on keeping, or has been dried artificially, as in the case of milled toilet soaps. Hard soaps containing less than that amount have been reduced intentionally, and may contain an excess of water or alkali, or any of that well-nigh endless number of adulterants that are incorporated with soap.

The determination of the **total alkali** in the soap can be conveniently combined with the determination of the fatty matter if an accurately measured volume of standard acid be used for decomposing the soap. The acid liquid is then filtered to remove traces of fatty acids, and the excess of acid is titrated back with standard alkali (see below).

The alkali is calculated in the case of hard soaps to caustic soda, Na_2O, and in the case of soft soaps to caustic potash, K_2O. Some hard soaps may contain small quantities of potash, but this is, as a rule, disregarded. More frequently soft soaps contain notable proportions of soda. If a separate determination of soda and potash be required, the soap must be decomposed with hydrochloric acid, and the potash in the acid liquid estimated as potassium platinic chloride in the usual manner. From the amount of potash so found, and from the quantity of acid required to neutralise the total alkali, the caustic soda is calculated. Of course, any other method used in mineral analysis may be employed.

(*b*) *Combined Alkali, Free Caustic Alkali, and Alkaline Salts*

The total alkali is the sum of the several amounts of alkali present in the soap as (1) *alkali combined* with fatty (and rosin) acids: combined alkali; (2) *free caustic alkali;* (3) *alkali as carbonate, silicate, or borate.*

1. *The Combined Alkali* is usually found by difference, *i.e.* by subtracting the sum of the amounts of alkali obtained for (2) and (3) from the total alkali as determined above. It can, however, be found direct by titrating the alcoholic solution of the soap with normal acid (see below) after neutrality has been established to phenolphthalein, using methylorange as an indicator. This may be done as a check, or in order to dispense with the determination of the alkali present as carbonate, silicate, and borate (3), which obviously can then be found by difference.

2. *Free Caustic Alkali.*—A preliminary test is made by dropping an alcoholic solution of phenolphthalein on a freshly cut surface of the soap. Pink coloration indicates presence of free caustic soda; and, if the soap be moist, also of carbonate, silicate, and borate. If the soap is dried out the alkaline salts do not redden the phenolphthalein. In order to separate free caustic alkali from the alkaline salts, a portion of the sample is dissolved in absolute alcohol and filtered. The alkaline salts remain on the filter, so that the alcoholic filtrate may now be tested with phenolphthalein.

Free caustic alkali should be absent from well-made soaps, especially from toilet soaps. As a great deal of circumspection and experience is required to so "fit" a soap that it contains practically no free alkali, most of the ordinary commercial soaps contain an excess of free alkali. If this be small, the free caustic soda will be converted on exposure to the atmosphere into carbonate, so that in many cases no free alkali will be found, especially if only the outer portions of a cake be tested. If, however, the excess of free caustic soda in a soap be large, as notably in scouring soaps and cheap toilet soaps made by the cold process, the detection of free alkali will offer no difficulty.

It should be borne in mind that under the term free alkali frequently all that alkali is understood which is not combined with fatty acids to form true soap, so that carbonate, silicate, and borate are included in "free alkali." I define here free alkali as free caustic alkali, thus differentiating it from the alkaline salts.

Free caustic alkali is determined quantitatively (*Hope*[1]) by dissolving 10 to 30 grms. of the sample in hot absolute alcohol in a loosely corked flask so as to prevent absorption of moisture from the air. Highly watered soaps must be first dehydrated to some extent, whilst access of carbon dioxide is excluded. The hot solution is filtered rapidly, taking care that no soap-jelly separates out on the filter; if the operation is carried out judiciously, a hot water funnel can be dispensed with.[2] The filter is washed with absolute alcohol, and the filtrate received in a narrow-mouthed flask. Phenolphthalein is then added, and the solution is titrated with decinormal hydrochloric acid. In some cases the alcoholic soap solution may exhibit an acid reaction to phenolphthalein. This acidity may be due to the soap containing, in consequence of faulty "fitting," an acid stearate (palmitate or oleate, cp. p. 76) or to fatty acids having been added to "kill" an excess of alkali. The amount of decinormal alkali required to neutralise the solution is calculated to *free fatty acids*, in terms of oleic.

3. The precipitate left on the filter contains *carbonate*, *silicate*, and *borate*, with which other insoluble substances, added as "fillers," such as starch, talcum, colouring matters, etc., may be admixed. (With regard to the *complete* examination of this precipitate see

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[1] *Chem. News*, 43 (1881), 219.

[2] *Spaeth* recommends to use Soxhlet's extractor (cp. *Journ. Soc. Chem. Ind.* 1896, 139), but in my opinion this is an unnecessary complication.

below.) To determine the alkali contained in the alkaline salts the precipitate on the filter is washed with cold water (see (*e*) 1). The alkali in the filtrate is determined by titration with standardised acid, using methylorange as an indicator. The acid used is calculated to Na_2O.

(*c*) *Determination of Water*

The direct determination of water in soaps is, as a rule, an unnecessary operation. In the case of genuine soaps it suffices for all practical purposes to calculate the fatty acids to anhydrides and add their weight to the amounts of alkali in its various forms. The water is then found by difference. Soaps reaching the analyst's laboratory have, as a rule, lost more or less water by drying; hence the direct determination of water in soaps does not afford a reliable means of valuation. For it must be remembered that ethereal oils volatilise with the water, as also alcohol (present in small quantities in some kinds of transparent soaps), and appreciable amounts of glycerol (present in notable quantities in soaps made by the cold process, as also in some toilet soaps). Moreover, if a soap contains considerable proportions of free caustic soda, part of the loss will be compensated by the absorption of carbon dioxide.

The direct determination of water is therefore only resorted to in exceptional cases. The soap is brought in fine shavings into a porcelain dish, weighed with a glass rod, so that the dry skin which prevents the escape of water from the inner portions can be conveniently broken up. This is especially necessary in the case of highly watered soaps.

For the purposes of valuing a sample of soap the determinations described under (*a*) to (*c*) will suffice. Further tests embrace the examination of the fatty matter, and detection and determination of other constituents of the sample.

(*d*) *Examination of the Fatty Matter* ("*Soap Stock*")

If no wax has been employed in the separation of the fatty matter, the separated fatty acids may be used direct for the following tests. Otherwise a fresh quantity of fatty matter must be prepared; the cuttings are most conveniently used up for this purpose.

The fatty matter may contain, besides *fatty acids*—

1. Rosin acids.
2. Neutral fat.
3. Unsaponifiable matter.

1. **Rosin Acids.**—Rosin acids are detected qualitatively by the *Liebermann-Storch* reaction (p. 393). For the quantitative estimation see p. 394.

2. **Neutral Fat.**—A well-made soap will but rarely contain unsaponified fat. If neutral fatty substances have been added intentionally to the finished soap, as in the case of "super-fatted" soaps (admixture with olive oil, etc., or in the case of certain toilet soaps, with wool wax), they will be obtained together with any unsaponifiable matter present and must be separated from it subsequently.

The neutral fat *plus* unsaponifiable may be isolated in a direct manner from the sample of soap by dissolving a weighed quantity in water or alcohol, adding standardised caustic potash to neutralise free fatty acids (if any), using phenolphthalein as indicator, and exhausting the soap solution as described Chapter VI. p. 293.

The residue from the ethereal solution consists of neutral fat *plus* unsaponifiable matter. The separation of the two constituents is effected by saponifying the mass and again extracting with ether.

If unsaponifiable matter be absent, the total ether residue consists of neutral fat; otherwise the neutral fat is found by difference, or may be found in a direct manner by isolating the fatty acids and calculating their amount to glycerides.

A complication arises if the soap contain wool wax. If the latter be suspected, the ether residue should be saponified with dilute alcoholic potash on the water-bath, so as to obtain part of the wool wax as unsaponifiable matter.

3. **Unsaponifiable Matter.**—This is isolated and estimated together with neutral fat as described. If no neutral fat has been found, the total ether residue consists of unsaponifiable matter. This is examined as described in Chapter IX.

In addition to the substances mentioned in Chapter IX. the presence of vaseline, paraffin oil, oil of turpentine, tar oils, naphthalene, petroleum, hydrocarbons, hydrocarbons from "distilled grease," etc. may be suspected.

Carnaüba wax, stated in some text-books as being usually admixed with soaps in order to render possible the incorporation of large proportions of paraffin oil, is not used in practice, as the same object can be attained by cheaper methods.

The examination of the FATTY ACIDS themselves, after separation from rosin acids, neutral fat, and unsaponifiable matter, with a view to determining the nature of the "stock," is a complicated problem, requiring systematic application of the methods described in the first volume of this work.

(*e*) *Substances insoluble in Alcohol*

The estimation of all those substances which are insoluble in alcohol is conveniently combined with the determination of the free caustic alkali described (p. 1077), by collecting the insoluble matter on a tared filter previously dried at 100° C., and weighing after drying at 100° C.

Good soaps yield but insignificant amounts of residue. Only the transparent soaps manufactured by the "alcohol process" will be absolutely free from insoluble matter.

The residue obtained on the filter may consist of—

1. Water-soluble substances, such as chloride, sulphate, carbonate, silicate, and borate of the alkalis.

2. Mineral substances insoluble in water, viz. colouring matters and "filling" and "weighting" substances, such as French chalk, etc.

3. Organic substances, especially starch, dextrin, gelatin (carrageen mucilage).

1. **Water-soluble Substances.**—The residue on the filter is washed with cold water so as not to dissolve any gelatin that may be present. The presence of silicate will have been noticed already in the determination of fatty matter when decomposing the soap by acid (see above under (*a*)). If the silicic acid has not been estimated in the same test in which the fatty matter has been ascertained (provided no other water-insoluble substance be present), it can be determined at this stage by acidifying the filtrate with hydrochloric acid after the total alkali present in it has been determined by titration, see (*b*) 3, and evaporating to dryness in the usual manner. The filtrate from the separated silica may be tested for boric acid.

If boric acid be absent, the carbonate *plus* silicate can be calculated from the alkali found by titration, and the silica found by weighing. If boric acid be present and the proportion of borate be required, the water-soluble portion is best divided into three parts. In one portion the carbon dioxide is estimated, in a second portion the silica, and in the third the total alkali is determined by titration.

Chlorides and *sulphates* are best determined in aliquot portions of the acid liquor, obtained after separating off the fatty matter as described in (*a*). It should be remembered that in that case nitric acid must be employed for decomposing the soap.

2. **The water-insoluble portion** is ignited, so as to burn off organic substances, and the residue weighed. The ash is examined qualitatively and quantitatively in the usual manner.

3. **Organic Substances.**—The microscopical examination of the total residue insoluble in alcohol may furnish useful indications. Thus *starch* will be detected. The microscopical examination may be corroborated by testing with iodine. If its quantitative determination be required, the starch is converted into glucose by washing the alcohol-insoluble residue on the filter with cold water to remove the water-soluble substances and *dextrin*, and boiling with dilute sulphuric acid, replacing the water as it boils away. The liquid is then neutralised with barium carbonate, filtered, and the glucose estimated by titration with *Fehling's* solution in the usual manner.

Dextrin has been washed out by cold water simultaneously with the soluble salts. The proportion of dextrin is estimated by precipitation with alcohol. This is done best in a small beaker, tared with a glass rod. The liquid is stirred vigorously, so that all the dextrin is made to adhere to the sides of the beaker. The aqueous liquid is then poured off, the dextrin washed with alcohol, and determined by weighing the beaker after drying at 100° C.

Gelatin is dissolved by washing the alcohol-insoluble residue with hot water. The filtrate is then tested with tannic acid.

(*f*) *Other Substances occurring in Soaps*

1. **Glycerol.**—The minute quantity of glycerol left in hard soaps, made by the "boiling process," can only be determined accurately if a large quantity of soap be employed. The glycerol passes into the aqueous liquid on decomposing the soap with mineral acid, and is determined as described under estimation of glycerol in spent soap lyes (p. 1089). The quantity of glycerol will indicate whether a hard soap has been made by the "cold process." In that case about 5 per cent of glycerol will be found. The *absence* of glycerol from soft soaps will prove that fatty acids have been used as "stock."

Considerable quantities of glycerol are intermixed with certain toilet soaps made by the milling process. On account of its cosmetic properties, the glycerol must be considered a valuable ingredient of such soaps. The glycerol in these soaps is determined by dissolving the soap in water, separating the fatty matter by a mineral acid, and filtering off. The filtrate is neutralised with barium carbonate, and boiled down to the consistence of a syrup. The residue is then extracted with a mixture of three parts of 95 per cent alcohol and one part of ether, the alcoholic solution filtered and evaporated on the water-bath to a small bulk, and finally dried under a desiccator. The glycerol in the crude glycerin thus prepared is determined by the acetin process (p. 286).

If also sugar be present in the soap, as in cheap transparent soaps, the sugar must be first removed (cp. below).

2. **Sugar** is found to a considerable extent (up to 25 per cent) in cheap transparent soaps. The determination of the saccharose is best effected by boiling the filtrate (or a measured portion of it) obtained in (*a*) with dilute sulphuric acid to invert the sugar, rendering alkaline, and heating with *Fehling's* solution after previous diluting so as to prevent oxidation of glycerol. The separated cuprous oxide is estimated in the usual manner and calculated to saccharose. If a considerable quantity of sugar be present it may be determined polarimetrically.

If glycerol and sugar be present conjointly, separation is effected, according to *Donath* and *Mayrhofer*,[1] by adding to the solution sufficient slaked lime to combine with the sugar present, admixing an equal quantity of washed and ignited sand, then boiling down to the consistence of a syrup, pulverising the residue after cooling, and exhausting in a corked flask with 80-100 c.c. of a mixture of equal volumes of alcohol and ether. The solution will then contain the glycerol (free from sugar), and may be estimated as described under 1.

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[1] *Zeit. analyt. Chem.* xx. 383.

3. **Carbolic Acid.**—The determination of "carbolic acid" (phenol and cresols) in carbolic soaps is carried out with sufficient accuracy by the following method (*Lewkowitsch*):—

Weigh off a somewhat large amount of the sample, say 100 grms., dissolve in hot water and add sufficient caustic soda to render the solution strongly alkaline. Then precipitate the soap by common salt, filter off the curdy soap, and wash the soap with brine. Boil down the solution which contains the phenol and cresols as sodium carbolate and cresylates, and precipitate any retained soap in the same manner. Filter again, boil down to a small bulk, and transfer the solution to a stoppered graduated cylinder of 50 or 100 c.c. capacity, add sufficient salt so that some remains undissolved, and acidify with sulphuric acid. The volume of the separated phenols is then read off and the number of c.c. taken as so many grams.

If greater accuracy be required the separated phenols may be brought into ethereal solution and recovered after distilling off the solvent. The phenol and cresols may then be determined by *Koppeschaar's* method.

In the valuation of **textile soaps**[1] the following points must be borne in mind:—

Soap intended for *scouring raw wool* should not contain free caustic alkali, as the free alkali acts injuriously on the wool, destroying its surface by pitting the scales and taking away its lustre.

Potash soap is preferable to soda soap, *cæteris paribus.* A small amount of alkaline carbonate is permissible if the raw wool is of inferior quality. Unsaponified fat, unsaponifiable matter, rosin, silicate, and "fillers" should be absent. "Secret powders" consist largely of sodium carbonate and inert substances with a minimum of palm oil soap.

Soaps for *scouring the woven woollen fabric* for best class goods should be devoid of free alkali. *Cæteris paribus,* a potash soap is preferable to a soda soap.

For the scouring of low class goods, such as union goods for which mungo and shoddy are used, strongly alkaline soaps are demanded by manufacturers, and a certain amount of free caustic alkali and alkaline carbonates is permissible. Silicate and rosin should, however, be absent; nor should the soap contain unsaponified fat or unsaponifiable substances.

Soaps for the use of *calico printers* should also be free from alkali, as this acts injuriously on the colour of the printed calico.

Soaps for scouring *silk* should be perfectly free from uncombined alkali, as even the smallest amounts are apt to damage the "feel" and lustre of the silk. Still, a small amount of potassium carbonate in the soap is stated to have a beneficial effect. These soaps are mostly made from olive oil.

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[1] Lewkowitsch, *Journ. Soc. Dyers and Colourists*, 1891, 42; *Journ. Soc. Chem. Ind.* 1891, 258.

3. METALLIC SOAPS—WATER-INSOLUBLE SOAPS

The insoluble soaps of the individual fatty acids have been described in Chapter III.

These soaps are prepared by double decomposition of the alkali soaps with aqueous solutions of metallic salts, or by heating the free fatty acids with the oxides or carbonates of the metals.

The metallic soaps are used for the most varied purposes in the arts. Thus a solution of **magnesium oleate** in petroleum ether is added to the organic solvents in the dry cleaning process of silk, to prevent spontaneous conflagration, the magnesium oleate increasing the conductivity of the solvent to such an extent that the generation of electric sparks is prevented when the silk goods are taken out of the solvent. **Aluminium soaps**, especially **aluminium oleate**, are employed as "oil thickeners." They are dissolved, with the aid of heat, in mineral oils, to impart to them a greater viscosity, or, as the term runs, to give them more "body."

Lead and **manganese** soaps are used as "driers" in the manufacture of boiled oils and varnishes (cp. p. 973).

Lead plaster consists chiefly of lead oleate. Lead plaster prepared from oleic acid is completely soluble in ether, whereas plasters made from natural oils and fats yield an ether-insoluble residue consisting of the lead salts of the saturated fatty acids.

Zinc, iron, nickel, cobalt, and **chromium** soaps are employed in the manufacture of coloured varnishes, as also for water-proofing leather and canvas. **Copper soaps** are used in the production of anti-fouling preparations.

In this class of soaps must be also included the **metallic resinates.** Lime resinate is largely employed in the manufacture of solid lubricants (p. 953). Manganese resinate and lead resinate are soluble in warm linseed oil; these two salts are therefore used as liquid driers (cp. 974). Copper resinate, like the copper salts of fatty acids, is used as a rust preventative and for painting ships.

For analytical purposes the metallic soaps are decomposed by means of a suitable mineral acid (hydrochloric, nitric, sulphuric), when the fatty acids are obtained as an oily layer, or if the salts be decomposed under ether (which is in many cases the most advisable course) in ethereal solution, and the metal passes into the acid solution. Both the fatty acids and the acid liquor are then examined in the usual way.

As has been pointed out already under the heading of "Driers," p. 975, the metallic soaps are soluble to some extent in petroleum ether, hydrocarbons, carbolic acid.[1] The metallic resinates dissolve

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[1] The solubilities of the metallic soaps of linseed oil have been studied by Vulté and Gibson, *Journ. Amer. Chem. Soc.* 1902, 215.

more readily in light coal-tar hydrocarbons than in petroleum ether.[1] The dissolution of the metallic resinates in coal-tar naphtha is assisted by dissolving in the naphtha a quantity of rosin equal in amount to that existing in the resinates. Thereby any free hydrate or carbonate of the metallic base is neutralised.

III. GLYCERIN MANUFACTURE

Whereas the chemically pure substance described in Chapter III., p. 131, is termed "glycerol," I comprise all those commercial products which contain glycerol in a more or less pure state under the name of "glycerin."

It has been pointed out already that glycerin is a by-product of the stearine-candle and soap industries. It is obtained in dilute aqueous solutions, which contain various impurities, depending on the manufacturing process. The purest raw material results from saponification by means of water or lime (magnesia); less pure is the raw material obtained in the acid saponification processes. The crude glycerin recovered from soap lyes may surpass in quality the crude material obtained in the acid saponification processes, or it may be still more impure in case fats and oils (of low quality) have been saponified by means of black-ash lyes. Modern processes of refining have, however, overcome the difficulties caused by the various impurities, so that, *e.g.*, chemically pure glycerin from soap-lyes cannot be distinguished from glycerins obtained by lime saponification. Glycerins vary in quality with the care exercised in the manufacture, so that some crude glycerins obtained from acid saponification processes retain some organic impurities which seem to have hitherto defied all attempts to remove them, as the writer has ascertained in the case of a number of "chemically pure" glycerins originating from that process.

The weak solutions are concentrated, and yield the commercial brands of **crude glycerins.**

1. CRUDE GLYCERIN

The composition of commercial crude glycerins varies considerably with the process of saponification from which they originate. Hence the following three qualities must be distinguished:—

(1) Crude Saponification Glycerin

This glycerin represents the best quality of the crude glycerins. It is obtained from the "sweet water" of the autoclave processes.

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[1] The solution of metallic resinates in coal tar hydrocarbons may be diluted with light petroleum spirit, which assists in the drying of the resinates. Truchot, *Journ. Soc. Chem. Ind.* 1897, 449.

According to the amount of water charged into the autoclave and to the quantity of steam sent into the autoclave during the saponification process, the proportion of glycerin in the "sweet waters" will vary from 6 to 16 per cent. The metallic oxides contained in the "sweet waters" are neutralised and the filtered solution is concentrated by means of steam, either in a Wetzel pan, as shown in Fig. 84, or as is done in modern works by means of a vacuum evaporator of identical or similar type to those shown in Figs. 85-88. According as the quantity of salts separating when the bulk of water has been driven off is considerable or not, a vacuum evaporator either of the type A or type B, Fig. 86, is used. The evaporation is carried on until the crude glycerin contains about 85-90 per cent of glycerol. Its specific gravity is then from 1·240 to 1·242, corresponding to the commercial brand of "28° Bé. saponification crude" or "candle crude" glycerin. The colour of this glycerin varies from yellow to dark brown; its taste is sweet. Tested with basic lead acetate it gives but a slight precipitate. By refining this crude glycerin with charcoal, a "refined" glycerin (used for a number of commercial purposes) is obtained. This crude glycerin contains from 0·3 to 0·5 per cent of ash, chiefly calcium (or magnesium) sulphate and small quantities of organic impurities.

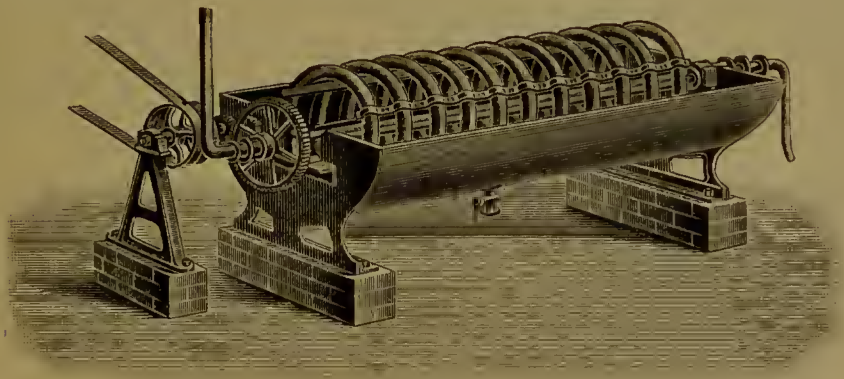

Fig. 84.

The valuation of this crude glycerin is carried out by determining the pure glycerol, the ash, and the organic impurities.

The percentage of *glycerol* is best ascertained by the acetin process; the oxidation methods, especially the bichromate method, being apt to lead to too high results (cp. p. 286), in case the glycerin contain some organic impurities which are not removable by the method of purification described below. Hence, although in some cases the acetin method and the bichromate method may lead to practically identical results, in most cases the determinations by the bichromate method will lead to too high numbers, especially so in the case of glycerins produced during the last few years, as shown by the following table:[1]—

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[1] Lewkowitsch, *Analyst*, 1903, 104.

Comparison of the Acetin and Bichromate Methods (*Lewkowitsch*)

Saponification Crude.	Acetin Method. Per cent.	Bichromate Method (Purified with Copper Sulphate). Per cent.
1	89·91 ; 90·75 ; 90·43	93·68 ; 94·21 ; 94·71 ; 94·90
2	90·69 ; 90·74	92·70 ; 93·08
3	94·02 ; 94·12	97·21 ; 97·94
4	85·23 ; 85·42	86·72 ; 86·41

The *ash* is determined by heating a few grams in a platinum dish, and weighing the residue obtained on incineration.

The *organic impurities* may either consist of fatty acids which have not been completely removed, or of other organic substances, the nature of which has not yet been defined. The fatty acids are detected by diluting one part of crude glycerin with three parts of water, and adding strong hydrochloric acid. A turbidity points to the presence of fatty acids. The organic impurities are determined quantitatively by allowing a few grams to evaporate gently at 160° C. and deducting from the weight of the residue the weight of the ash found on incineration. The amount of organic residue gives a fair indication as to the care with which the glycerin has been manufactured. As a rule, the quantity of organic impurities lies below 1 per cent.

The test for *arsenic* (see p. 1111) completes the chemical examination of the crude glycerin.

(2) CRUDE DISTILLATION GLYCERIN

This glycerin is recovered from the acid waters resulting in the acid saponification processes, and is termed commercially *crude distillation glycerin*, since the fatty acids obtained in the process must be distilled to yield candle material. The dilute glycerin waters are worked up in the same manner as described under (1), but owing to the large amount of sulphuric acid, a considerable amount of salts is retained after neutralisation of the mineral acid with lime. With the progress of concentration, especially when the crude glycerin approaches the specific gravity 1·240, sulphate of lime, which can no longer be held in solution, drops out and is deposited on the heating surface of the evaporating apparatus in the form of a hard crust, which rapidly diminishes the evaporative power of the apparatus unless the calcium sulphate is removed. Hence, ordinary tube evaporators, such as are represented by vessel B in Fig. 88, are useless for concentrating the dilute solutions. A type of evaporator must be employed which permits the heating surface to be continuously kept clean. Such an evaporator is shown in Fig. 85 ; the inner construction is exemplified by the Figs. 86 and 87.

The finished crude glycerin contains as much calcium sulphate as the glycerol is capable of holding in solution (cp. p. 133). The ash of crude "distillation glycerin" reaches therefore as much as 2-3·5 per cent. The amount of organic impurities is also greater than in the crude "saponification glycerin"; according to the care exercised in the manufacture, it may rise to several percents. The colour of this crude glycerin is usually pale yellow; its taste is sharp and astringent, and it emits an unpleasant smell when rubbed between the hands. A voluminous precipitate is obtained with basic lead acetate; on addition of hydrochloric acid a turbidity, due to fatty acids, appears.

The specific gravity of this crude glycerin is the same as that of the saponification glycerin, viz. 1·240-1·242; it contains, as a rule, from 84 to 86 per cent of glycerol. It is known in commerce as "distillation glycerin, 28° Bé."

The glycerol in this glycerin should be determined by the acetin process in preference to the bichromate method. The differences in the percentage, as obtained by the two methods, is still greater than in the case of saponification crude, owing to the larger amount of organic impurities. This has been specially shown by *Lewkowitsch* [1] by a few examples reproduced in the following table:—

Comparison of the Acetin and Bichromate Methods (*Lewkowitsch*)

Crude Distillation Glycerin.	Acetin Method. Per cent.	Bichromate Method (Purified with Copper Sulphate). Per cent.
1	86·26 ; 86·16 ; 86·22	89·70 ; 89·22
2	83·51 ; 83·68	89·44 ; 89·73
3	83·1 ; 82·98	83·9 ; 83·56 ; 83·52

The ash and the organic impurities are determined as described above (p. 1086).

(3) SOAP-LYE GLYCERIN, SOAP CRUDE GLYCERIN

The lyes obtained in the soap-making process by boiling the glycerides in an open pan contain practically all the glycerin the natural oils and fats are capable of yielding. According to the manner in which the "changes" of soap lyes are worked up by the soapmaker the spent lyes may contain from 5 to 8 per cent of pure glycerol. Besides glycerol, the spent soap lyes hold in solution the common salt used in "cutting" the soap and small amounts of free caustic soda, sodium carbonate, and soap.

The specific gravities of the spent lyes vary, as a rule, from 1·08 to 1·14, according to the amount of salt dissolved by them.

The value of spent soap lyes depends on their percentage of

[1] *Analyst*, 1903, 106.

glycerol, and on their comparative freedom from free caustic alkali and sodium carbonate.

A works' chemist usually determines the proportion of *glycerol* by closely simulating the method of purification and recovery practised in the soap works. In commercial analysis, provided sulphur compounds be absent, 1000 grams are heated to boiling and are acidified with hydrochloric acid, when fatty acids, etc., separate as an oily layer on the top. This is filtered off, the filtrate is made neutral and lead acetate added. The precipitate is filtered off and the clear solution boiled down. The salt which separates is scooped out with a spoon and sucked dry by means of a filter-pump. When a few c.c. of solution are left finally, this is added to the salt, and the latter exhausted with a mixture of three measures of methylated spirit and one measure of ether. The alcoholic filtrate is evaporated down on the water-bath and the crude glycerin thus obtained examined by the acetin method.

In a factory where the purification of the soap lye is closely adapted to the works' process, the determination may be shortened (*Lewkowitsch*[1]) by evaporating the ether-alcoholic solution on the water bath and then rapidly heating to 150° C., weighing, burning off the glycerin, and weighing again. The difference corresponds to the contents of pure glycerol. In my own practice, when I closely follow the manufacturing process, this abbreviated method, based on a series of experiments carefully checked by the acetin method, gives very satisfactory results.

If but small quantities of soap lye are available, so many grams are weighed off as will approximately correspond to 1·2 grms. of pure glycerol, and the glycerol is then determined by *Hehner's*[2] bichromate method.

The following standard solutions are required:—

1. Solution of potassium bichromate containing 74·86 grms. of $Cr_2O_7K_2$ per litre.[3] The exact oxidising value of the solution must be checked by titration with a standardised solution of ferrous sulphate or of pure ferrous ammonium sulphate or of pure iron wire.
2. Solution of ferrous ammonium sulphate containing about 240 grms. per litre.
3. Bichromate solution, ten times more dilute than solution 1.

The ferrous solution is exactly standardised upon the stronger bichromate solution, 1 c.c. of which should correspond exactly to 0·01 grm. of glycerol.

The soap lye is slightly diluted, and if it contain notable quantities of soap, is acidified with sulphuric acid; the fatty acids, etc., are filtered off and the filtrate is then purified by means of lead acetate, or by means of caustic potash and copper sulphate, filtered, and made up to 100 c.c.

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[1] *Analyst*, 1903, 106. [2] *Journ. Soc. Chem. Ind.* 1889, 6.

[3] Hehner recommends to add 150 c.c. of strong sulphuric acid before making up to 1000 c.c., but I consider it safer to keep the not acidified bichromate solution in stock, and to add the sulphuric acid when the actual test is carried out.

25 c.c. of this solution are then run into a beaker previously cleaned with bichromate solution and concentrated sulphuric acid, and 40 c.c. of the concentrated potassium bichromate solution are run in. As the bichromate solution is necessarily a strong one, the measuring must be done with the greatest care, and attention must be paid to the temperature of the solution. *Hehner* states that the strong bichromate solution expands 0·05 per cent for each degree C. I avoid the necessity for corrections by bringing the standard solutions to the normal temperature in a large water-bath, and keeping them thereat until the titration is finished.

25 c.c. of concentrated sulphuric acid are added, the beaker is covered with a watch-glass and heated in boiling water for 2 hours.[1] The excess of bichromate is titrated back with an excess of the ferrous ammonium sulphate solution, and the excess of the latter is ultimately measured by titration with the dilute bichromate solution, using potassium ferricyanide as an indicator.[3]

In case the lyes are properly purified, the acetin method leads to results practically identical with those obtained by the bichromate method. If, however, the impurities are not completely removed, then here also the bichromate method yields too high results. This is clearly shown by the numbers given in the following table. Those lyes, the specific gravity of which exceeds 1·2, represent partially concentrated lyes; all other lyes are original spent soap lyes.

Comparison of the Acetin and Bichromate Methods for determining the Percentage of Glycerol in Soap Lyes (Lewkowitsch).

No.	Specific Gravity.	Free Alkali, as Na_2O.	Glycerol Per Cent.	
			1000 c.c. Method.	Bichromate Method (purified with Copper Sulphate).
		Per cent.		
1	1·120	2·39	5·86	6·62 ; 6·80
2	1·114	0·58	7·36	8·48 ; 8·43
3	1·216	...	5·70	5·89 ; 5·81
4	1·1025	0·927	6·69	7·45 ; 7·33
5	1·0975	0·452	5·90	5·90 ; 6·09
6	1·1050	0·678	5·25	5·34 ; 5·43
7	1·0925	0·809	6·10	5·92 ; 5·88
8	1·1025	1·6	5·64	5·65
9	1·095	0·863	6·95	6·92 ; 6·93
10	1·2025	1·933	9·75	9·68 ; 9·67
11	1·0925	0·51	6·96	6·95 ; 7·07
12	1·09	0·768	6·62	6·78 ; 6·42
13	1·085	0·657	5·70	5·42 ; 5·45
14	1·22	...	11·57	12·5 ; 12·6
15	...	0·49	3·57	4·59
16	...	...	7·55	7·66 ; 7·69

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[1] Richardson and Jaffé (*Journ. Soc. Chem. Ind.* 1899, 331) consider 20 minutes sufficient. They also shorten the process by dispensing with the dilute bichromate solution.

Fanto[1] proposed to determine the glycerin in soap lyes by the iso-propyl-iodide method (p. 288). For reasons detailed above (p. 288) this method cannot be recommended, since the large amount of impurities contained in soap lyes, which may reduce the hydriodic acid, cannot readily be removed.

On the large scale the spent soap lyes are subjected to a process of purification consisting in the removal of fatty acids, rosin acids, and other organic impurities; the purified liquor contains salt and practically pure glycerol. This solution may be evaporated until the "salting point" is reached in fire-heated vessels or in tube evaporators, such as are used in sugar works, without fear of damaging the heating surface by deposition of salt. The "salting point" is marked by the lyes having acquired the specific gravity of 44° Tw. at 15·5° C. If evaporation is carried beyond this stage, salt will be deposited, whilst the specific gravity and percentage of glycerol gradually rise. The vessels in which the evaporation beyond the specific gravity of

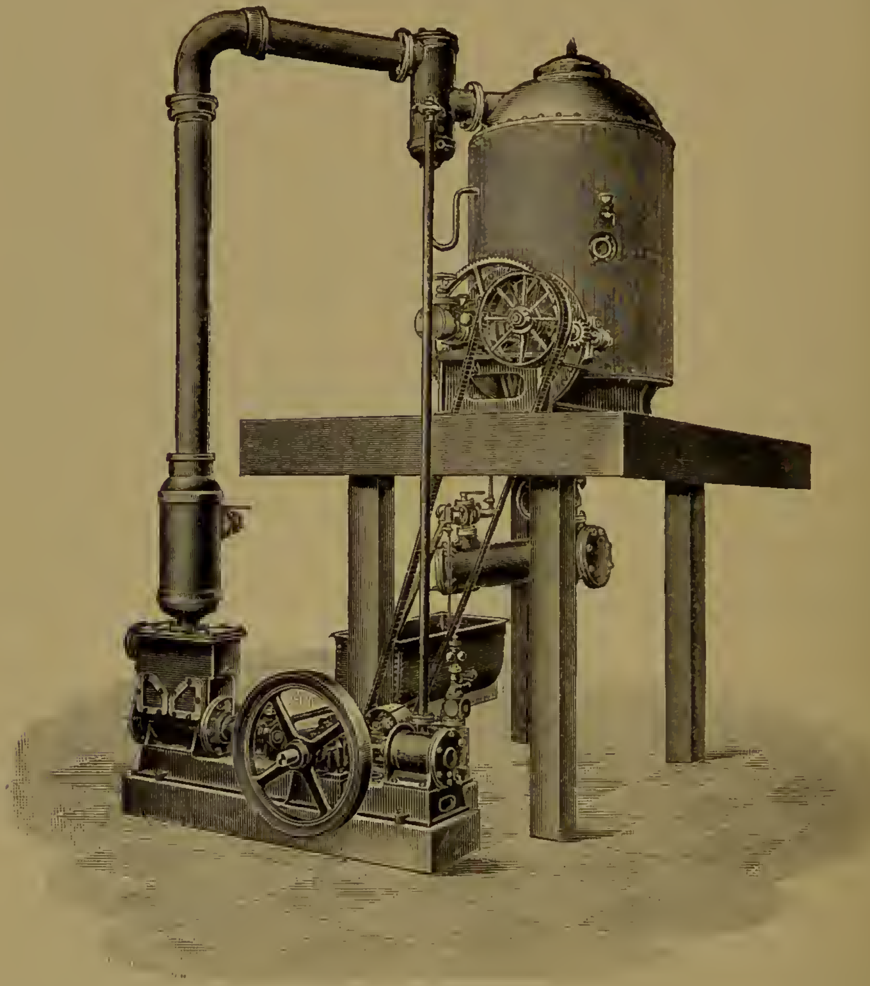

Fig. 85.

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[1] *Zeit. angew. Chem.* 1903, 413.

44° Tw. is carried on, must therefore be provided with suitable stirring and scraping arrangements to remove the salt as it separates, all tube evaporators being liable to incrustation with salt and gradual stopping up of the heating tubes.

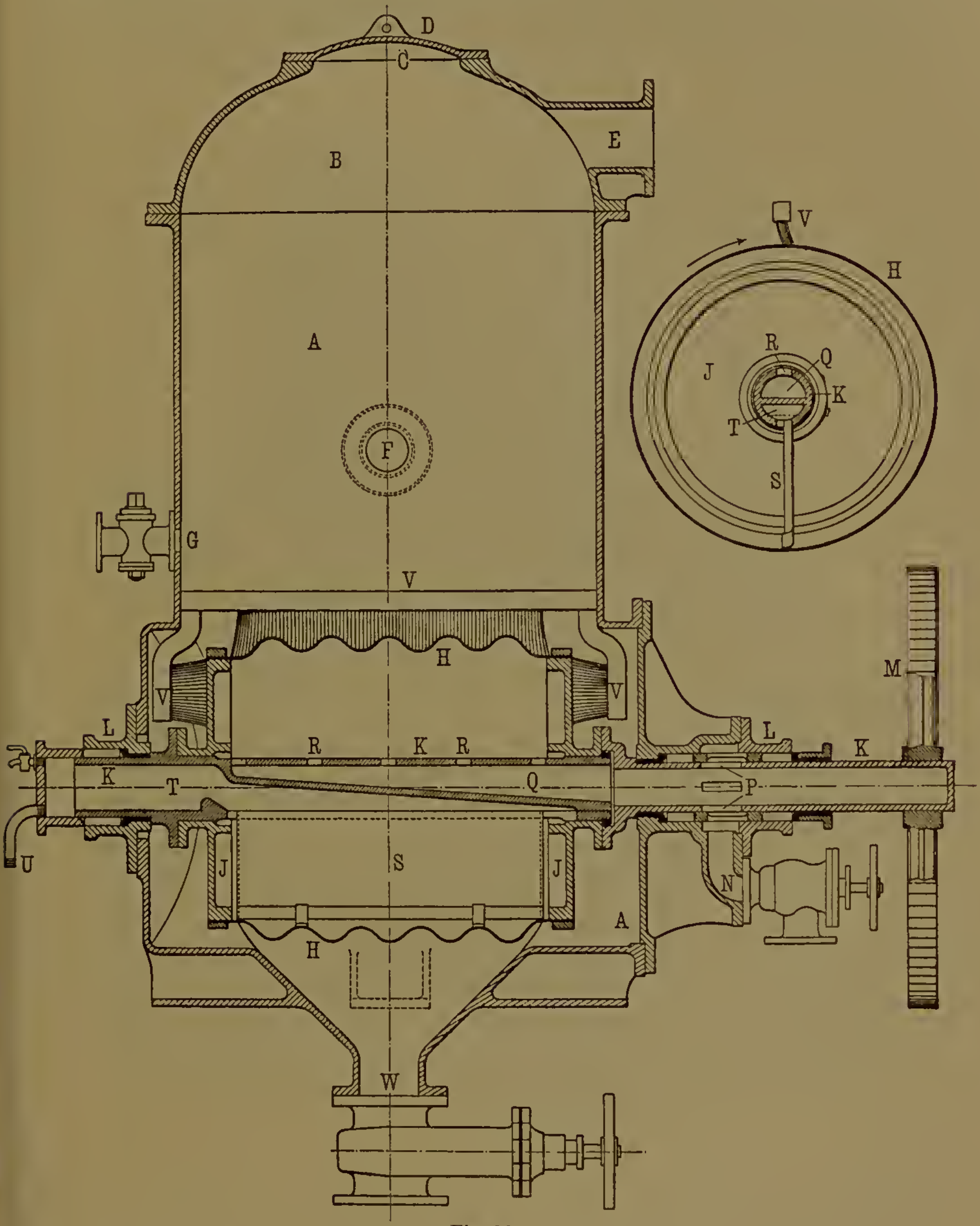

Fig. 86.

An evaporator which has been found suitable in practice for the concentration of lyes to the finishing point, *i.e.* until they reach the specific gravity of 1·3, has been designed by *Lewkowitsch*. It is shown in Fig. 85. Two types of the internal heating surface are illustrated by Figs. 86 and 87.[1] In these evaporators the soap lyes

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[1] Cp. English Patents, No. 28,747, 1897; No. 30,616, 1897.

are evaporated from the dilute state beyond the "salting point," the salt which falls out being removed by the aid of the vessel fixed at the bottom of the evaporating pan. This vessel can be emptied whilst the contents are kept continuously boiling. In large installations the lyes may be concentrated in double effet or triple effet vacuum apparatus. A double effet designed by the writer on the same principle is illustrated by Fig. 88. This shows a combination of the tube evaporator B with the evaporator illustrated by Figs. 85, 86, and 87. The first preliminary concentration up to the "salting point" is carried out in vessel B, whilst the further concentration takes place in vessel A. The finished glycerin —salt crude glycerin, soap-lye glycerin—has a specific gravity of 1·3. It usually contains 80 per cent of pure glycerol, about 10 per

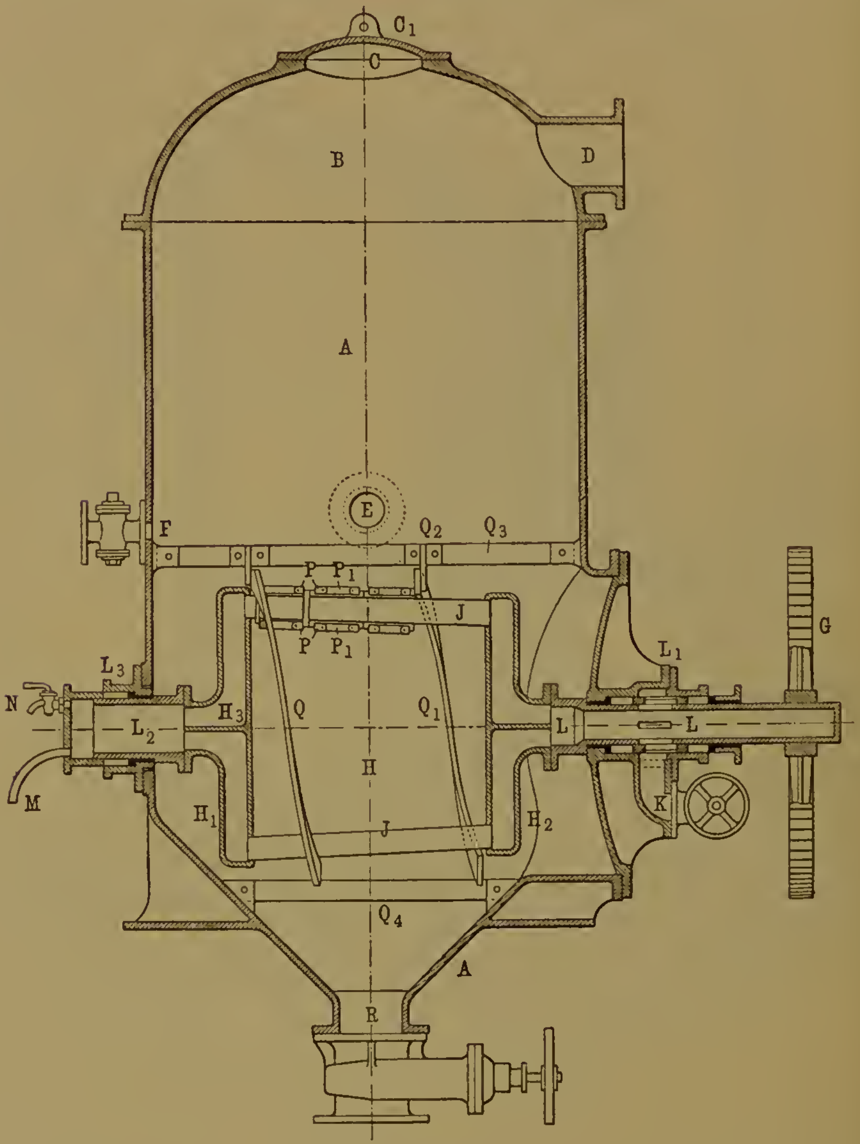

Fig. 87.

cent of salt, the remainder consisting of water and a small amount of organic impurities.

The salts in crude soap-lye glycerin should consist preponderantly of common salt. In impure crude glycerins sodium carbonate, caustic soda, sodium sulphate, sodium sulphite, sodium sulphide, sodium thiocyanate, and sodium thiosulphate are also found. The proportion of *organic impurities* in soap-lye glycerin varies considerably, depending on the process of purification used, etc. Some commercial glycerins contain less than 1 per cent of organic impurities (thus representing a glycerin of better quality than "distillation glycerin"), others, again, contain large quantities of impurities, consisting of fatty acids, rosin acids, and albuminoid substances, gelatin, and hydrocarbons (from bone fat). The colour of this crude glycerin is pale yellow to brown or almost black, according to purity. The taste of good samples is sweet, qualified, of course, by the common salt; impure

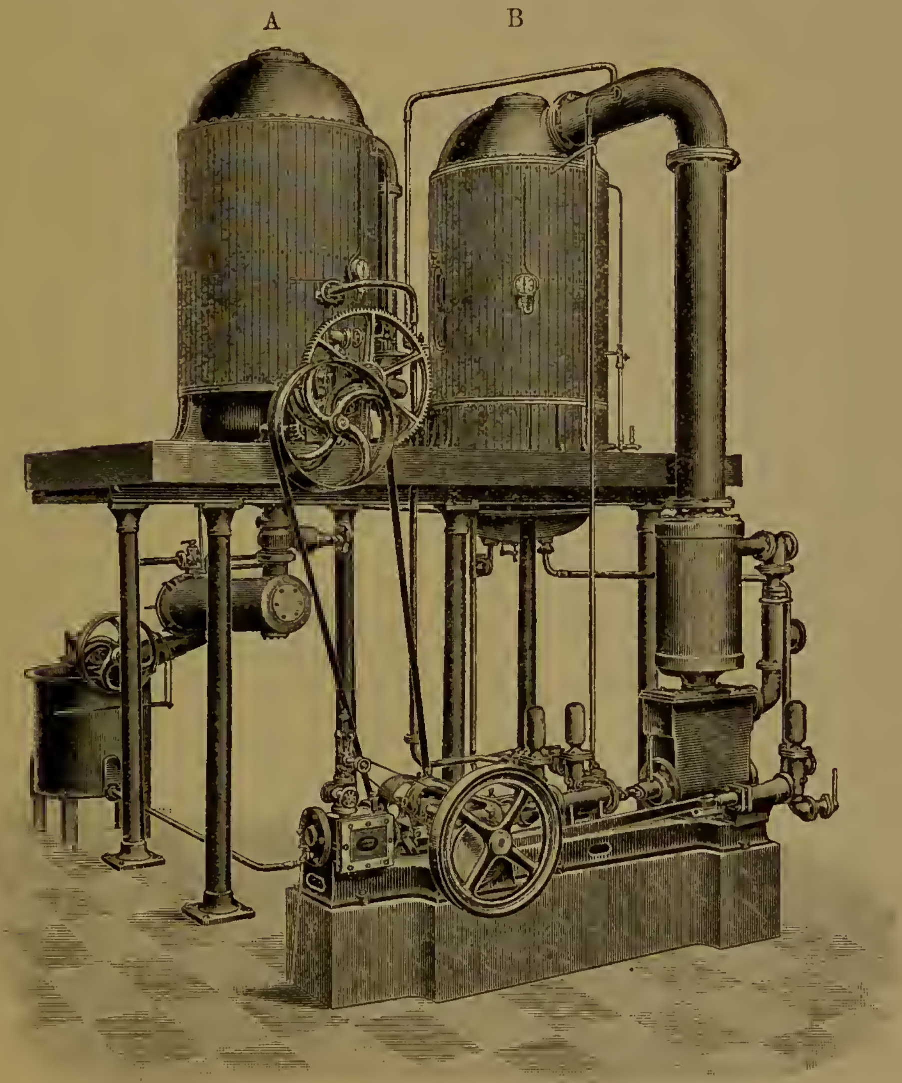

Fig. 88.

samples have a most unpleasant garlic-like taste, even if sulphides be absent.

Soap-lye glycerin can be rapidly distinguished from saponification as also from distillation glycerin by the large proportion of common salt (heavy precipitate with silver nitrate), and by its high specific gravity.

A soap-lye glycerin containing considerable quantities of sulphides, thiosulphates, or sulphites, is almost valueless to the refiner of crude glycerin.

The determination of *glycerol* is best carried out by the acetin method.[1] The bichromate method as described by *Hehner*[2] has been extensively used in commercial analysis. The procedure is briefly as follows :—

About 1·5 grms. of crude glycerin are weighed off in a 100 c.c. flask, and silver oxide added to remove the chlorine of the sodium chloride and to oxidise aldehydes. · A little water is then run in and the mixture allowed to stand for ten minutes. Basic lead acetate is added next in slight excess, and the volume made up to 100 c.c. A portion of the solution is filtered through a dry filter, and 25 c.c. of it placed in a beaker previously cleaned with concentrated sulphuric acid and bichromate solution, and treated as described above, p. 1088.

In the case of fairly pure soap-lye glycerins the silver oxide may be replaced by copper sulphate.

Although *Hehner* has shown by a number of comparative experiments, using both the acetin and the bichromate methods, that the results agree very well, and although the writer confirmed this in the second edition of this work,[3] this no longer holds good at present. For recently *Lewkowitsch*[4] proved by a large number of experiments that in the case of many crude glycerins the bichromate method yields appreciably higher results than the acetin method. This is shown by a number of analyses collated in the following table :—

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[1] Lewkowitsch, *Chem. Zeit.* 1889, 93, 191, 659 ; *Journ. Soc. Chem. Ind.* 1890, 479.

[2] *Journ. Soc. Chem. Ind.* 1889, 6.

[3] Cp. Lewkowitsch, *Chemical Analysis*, etc. 1898, p. 808.

[4] *Analyst*, 1903, 104.

[TABLE

Comparison of the Acetin and Bichromate Methods for determining the percentage of Glycerol in Soap Crude Glycerin (Lewkowitsch).

Description.	Acetin Method.	Bichromate Method (purified with Copper Sulphate).	Bichromate Method, purified with Silver Carbonate and Basic Lead Acetate.
Soap-lye crude .	86·66	86·45	
,, ,,	86·15 ; 86·06	86·01 ; 86·34	
,, ,,	75·02	75·38 ; 75·10	
,, ,,	80·51 ; 80·66	80·37 ; 80·04	
,, ,,	78·93	79·41	
,, ,,	85·94	85·43	
,, ,,	79·84	79·23	
,, ,,	83·05 ; 83·07	83·99 ; 84·65	
,, ,,	78·48 ; 78·55 ; 78·89	81·42 ; 81·60 ; 81·23	
,, ,,	80·46 ; 80·82 ; 80·28 ; 80·61	82·56 ; 83·03 ; 83·23 ; 83·89	
,, ,,	76·56 ; 77·45	79·36 ; 79·01	
,, ,,	81·44 ; 81·19	82·51 ; 82·61	
,, ,,	81·42	82·21	
,, ,,	79·13	81·52 ; 81·94	
,, ,,	75·20	78·79	
,, ,,	72·98	76·04	
,, ,,	72·01	77·44	
Last crude, concentrated further .	74·73	78·35	
Soap-lye crude .	77·31	77·96 ; 78·60	78·30 ; 78·33 ; 78·69
,, ,,	76·53 ; 76·61	78·17 ; 78·24	79·25 ; 79·53

The acetin method is all the more commendable for the valuation of soap crude glycerin, inasmuch as polyglycerols (residues from the glycerin stills) if admixed with crude glycerin, would be oxidised by the bichromate, and thus calculated to glycerol, whereas the polyglycerols are not converted into esters on boiling with acetic anhydride. Thus *Lewkowitsch*[1] has proved that soap crude glycerins containing polyglycerols show less than 80 per cent in the acetin test. The following table reproduces some analyses.

	Glycerol by Acetin Method. Per cent.
Soap Crude I. containing Still Residues .	76·20 ; 76·16 ; 76·45 ; 76·57
,, ,, II. ,, ,, ,, .	77·94 ; 77·68 ; 77·77 ; 77·76
,, ,, III. ,, more Still Residues	61·40 ; 61·38 ; 61·43 ; 61·09

Ash.—3-5 grms. of the sample are weighed off accurately in a platinum dish, which is placed at some distance over a small burner, and the glycerol allowed to evaporate off slowly. More heat should only be applied after the glycerol has been driven off, when a bulky carbonaceous residue is obtained. This is heated to a temperature sufficient to carbonise the organic matter, taking care that no sodium

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[1] *Chemiker Zeitung*, 1889, 659.

chloride is volatilised. After cooling, the charred mass is exhausted with water, transferred to a filter, and the filtrate boiled down in the platinum dish on the water bath. The residue, which must be white, is heated (not above 400° C. to avoid loss by volatilisation of sodium chloride), and weighed. The carbon on the filter may as a rule be disregarded. *Vizern*[1] recommends to also burn away the carbon; this may be necessary if the sample contain lime.

Richmond[2] proposed to estimate the ash by carbonising, as described above, adding a little concentrated sulphuric acid, heating over a Bunsen flame until the ash is burnt white, and multiplying the "sulphated" ash by 0·8. This method is not accurate, and cannot be recommended.

Organic impurities are determined as described page 1109. The drying at 160° C., until constant weight is obtained, requires a somewhat prolonged time. The process is shortened by adding to the residue, from time to time, a few drops of water.

Fatty acids are detected by acidifying the diluted glycerin with hydrochloric acid.

Arsenic is tested for as described page 1111.

The detection of sulphides, sulphites, and thiosulphates in the glycerin is of importance for purposes of valuation. Presence of *sulphides* is ascertained by testing with paper saturated with alkaline lead nitrate solution. To detect traces of sulphides down to $\frac{1}{100000}$th part (*Ferrier*)[3] a few c.c. of the solution are placed in a small flask, four or five drops of hydrochloric acid added, as well as a pinch of sodium bicarbonate, the liquid heated carefully to boiling, and a paper moistened with alkaline lead nitrate held over the flask.

Thiosulphates and *sulphites* are detected by treating the diluted glycerin with a few c.c. of a solution of barium chloride and filtering off the precipitate containing carbonate, sulphate,[4] and *sulphite*. To the clear filtrate two or three drops of hydrochloric acid and a few drops of a potassium permanganate solution are added. If the glycerin contains even less than $\frac{1}{10000}$th part of thiosulphate, a distinct turbidity is produced.

The detection of *sulphites* is effected by washing the precipitate on the filter with boiling water, stirring it up with a little water, and adding to this mixture starch solution and a few drops of iodine solution. In the presence of sulphites the blue colouration disappears with more or less rapidity, whilst in their absence the blue colour is permanent.

Another method to detect sulphides, sulphites, and thiosulphates in presence of sulphates (which may occur in soap lyes) has been proposed by *Browning* and *Howe*.[5] The solution should be made *slightly* alkaline; zinc acetate is then added in distinct excess. The precipitate of zinc sulphide is filtered off and tested by treating with

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[1] *Journ. Chem. Soc.* 1890, Abstr. 835.

[2] *Journ. Soc. Chem. Ind.* 1889, 7.

[3] *Journ. Soc. Chem. Ind.* 1893, 471.

[4] Dobbin, *Pharm. Journ.* 1900, 182, has shown that small quantities of barium sulphate are soluble in the presence of considerable amounts of thiosulphate.

[5] *Zeit. f. anorg. Chemie*, 1898, 371.

mineral acid. The filtrate is acidified with acetic acid, and the sulphates precipitated by barium chloride. To the filtrate iodine solution is added, until a permanent colouration is obtained; the excess is removed by stannous chloride and a few drops of hydrochloric acid (to prevent formation of basic stannic salts). If a precipitate is obtained at this stage sulphites are present. These are filtered off, and the filtrate treated with bromine water. The solution is again decolourised with stannous chloride; a precipitate would indicate presence of thiosulphates.

For the quantitative estimation of sulphides, sulphites, thiosulphates, and sulphates in presence of each other the reader must be referred to the original papers given in the footnote.[1]

2. DISTILLED GLYCERIN—DYNAMITE GLYCERIN

These glycerins are obtained from the crude glycerins described above, by distillation. The distilled glycerin is used for various purposes in the arts (for filling gas-meters, manufacture of inks, printers' rollers, etc.) The bulk of the distilled glycerin is employed in the manufacture of high explosives, such as dynamite, blasting gelatine, cordite, etc.

As these glycerins are obtained by distillation, they contain a very small amount of ash, and are thereby easily distinguished from crude glycerins. Distilled glycerins are further differentiated from crude glycerins by not giving a precipitate with lead acetate.

The commercial distilled glycerins vary in colour from yellow to white; they also vary in their content of glycerol, according to their specific gravities, which vary between 1·220 and 1·260.

The percentage of *glycerol* may be ascertained with approximate accuracy by referring to the tables of specific gravities given on page 1102. The small amount of ash these glycerins contain has a slight influence on the specific gravity. If great accuracy be required, the glycerol may be determined by the acetin method or the bichromate method, although it must be again repeated that the bichromate method has a tendency to yield too high results.

Dynamite glycerin represents in commerce that quality of distilled glycerin which has a specific gravity of 1·261 to 1·263. According to the care with which it has been manufactured, its colour varies from yellow to light straw colour.

Owing to the risks to which a manufacturer of dynamite is exposed if the glycerin be impure, the conditions to which a dynamite glycerin should conform are usually laid down in contracts between buyer and seller. Thus the following points are stipulated:—

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[1] Lunge and Smith, *Journ. Soc. Chem. Ind.* 1883, 463; Richardson and Aykroyd, *Ibid.* 1896, 171; Lunge and Segaller, *Ibid.* 1900, 221.

Specific Gravity.—This should be not less than 1·261 at 15·5° C. For its determination see p. 1104. This is a very important test, as high percentage of glycerol found by the bichromate method, or even by the acetin test, may be caused by presence of trimethylene-glycol, the occurrence of which has been proved in a sample of commercial glycerin obtained from low-class fats (*Noyes* and *Watkin*[1]). Presence of trimethylene-glycol may be suspected if low specific gravity is found concurrently with an apparently high percentage of glycerol. *Barton*[2] proposes to heat the glycerin to 225°-230° C. for two hours and then again to take the specific gravity, which he terms "permanent specific gravity." Thereby any hydrocarbons in glycerins from bone fat are volatilised. The "permanent specific gravity" will always be higher than the specific gravity of the sample, as the last traces of water will become volatilised; also trimethylene-glycol (boiling point 214°-217°) will most likely be driven off.

Lime, *Magnesia*, and *Alumina* should be absent.

Chlorine.—Traces only are permissible; the glycerin must not become milky with silver nitrate. Milkiness is observed when the proportion of sodium chloride lies between 0·025 and 0·01 per cent, as I have ascertained by a number of experiments. The quantitative determination of sodium chloride is, however, unnecessary.

Arsenic.—Only minute traces are tolerated. The test is made by making the glycerin *just* alkaline with a minute quantity of ammonia, and adding silver nitrate. No yellow precipitate must appear. This precipitate being soluble in ammonia, an excess of the latter must be avoided. Greater certainty is obtained by *Gutzeit's* reaction (see p. 1111), using mercuric chloride.

Organic Impurities.—The glycerin must not become brown or black within ten minutes after the addition of a few drops of silver nitrate to the diluted glycerin.

Total Residue.—This is determined as described p. 1110. It must not exceed 0·25 per cent of the dynamite glycerin.

Free Acids.—The glycerin should not be acid to litmus, nor should it contain fatty acids; the test for volatile fatty acids is carried out as described under chemically pure glycerin, p. 1109. Some specifications stipulate that on passing nitrous acid fumes through the glycerin, it must not curdle, it being supposed that oleic acid would thus be detected. It will be found more suitable to add hydrochloric to one volume of glycerin diluted with two volumes of water; a turbidity would indicate presence of insoluble fatty acids.

Nitration and Separation Test.—A sample of glycerin may prove good in all preceding tests, and yet be totally unfit for the manufacture of nitroglycerin. The suitability of a sample of dynamite glycerin must therefore be determined by the following process, which simulates large scale operations.[3]

375 grms. of a mixture, consisting of one part (by weight) of nitric acid, specific gravity 1·5, and two parts (by weight) of sulphuric

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[1] *Journ. Soc. Chem. Ind.* 1896, 207.

[2] *Ibid.* 1895, 516.

[3] Lewkowitsch, *Chemiker Zeitung*, 1895, 1423; *Journ. Soc. Chem. Ind.* 1895, 1073.

acid, specific gravity 1·845, previously cooled down to the ordinary temperature in a closed vessel, are weighed off in a beaker of about 500 c.c. capacity. A thermometer, used during the nitration as a stirrer, is then introduced into the acid, and the beaker immersed in a capacious vessel filled with cold water, or, if necessary, with ice. A stream of cold water is kept running through the vessel by means of a stout india-rubber tubing, say $\frac{3}{4}''$ diameter, coiled at the bottom of the vessel. It is very important that the india-rubber tubing should be securely fastened to the water-tap, if the latter be near the operator, as it may easily happen that the tube is thrown off the tap by the pressure of the water in the pipe, when any water accidentally coming into contact with the acid may raise the temperature to such a point that explosion will ensue. I use, therefore,[1] thin-walled beakers, so that they may be rapidly broken in case the temperature rises to a point of danger; the rapid discharge of the mixed acids and nitroglycerin into the large mass of water will then effectively prevent an explosion.

When the temperature of the acids has fallen to about 12° to 15° C. 50 grms. of the sample of glycerin, weighed off in a beaker having a spout, are allowed to fall into the acids, drop by drop, constantly stirring with the thermometer, and observing the temperature after the addition of every single drop of glycerin. Considering the danger attending this operation, the inexperienced analyst should be instructed in the carrying out of the test by an experienced operator. If this be not feasible, the safest plan will be to proceed in the manner described, *i.e.* add cautiously drop by drop, stirring all the while, so that no overheating may take place *locally*, and never allowing the temperature to exceed 30° C. No addition of another drop of glycerin must be made until the temperature has fallen below 25° C. (An experienced operator will, of course, proceed a little more rapidly.)

If all the glycerin has been dropped in in this manner, the mixture is stirred for a short period, until the temperature has fallen to about 15° C., and then transferred to a separating funnel, which must be absolutely dry. The safest plan is to rinse the funnel with concentrated sulphuric acid.

If the dynamite glycerin is of good quality the nitroglycerin will rapidly rise and separate in a few minutes as an oily, somewhat turbid layer on the top of the spent acids. The quicker the separation into two well-defined layers takes place the better is the glycerin. If flocculent matter be noticeable in the nitroglycerin layer, if the separation be slow, and an intermediate layer of this flocculent substance render the line of separation indistinct, the sample is unsuitable for dynamite making. In some cases, owing to the nitroglycerin being honeycombed with this flocculent substance, some hours are required for separation. Such a glycerin must, of course, be rejected.

Considering the somewhat dangerous nature of this test in an

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[1] Lewkowitsch, *Chemiker Zeitung*, 1895, 1423; *Journ. Soc. Chem. Ind.* 1895, 1703.

analyst's laboratory, the quantity of glycerin employed has been gradually reduced from 50 to 15 grms. This should, however, be the lowest permissible quantity, as the indications furnished by the nitration test become unreliable if only 10 grms. of glycerin be used.

The *quantitative* determination of the yield of nitroglycerin is conveniently combined with the nitration test. In that case the accurate quantity of glycerin employed is either determined by weighing the empty beaker, or the beaker is rinsed out with the mixture of acids and nitroglycerin. The former method is the safer one. After separation of the nitroglycerin the acid layer is carefully drawn off, and the nitroglycerin slightly agitated without shaking, so that any drops of acid adhering to the vessel are brought into one mass. This is carefully drawn off, and the nitroglycerin washed with water of 35°-40° C. once, then once or twice with a 20 per cent solution of sodium carbonate, and then again with water. The nitroglycerin is next transferred to a suitable burette, in which the adhering water rises to the top. The volume is read off, and the quantity determined by multiplying the number of c.c. by 1·6, the specific gravity of nitroglycerin (the specific gravity of the product may be determined, if desired), or by weighing the product after separation from water by filtering over salt.

It is evident that this process yields only approximate results, especially so as nitroglycerin is slightly soluble in water. The method is, however, satisfactory for the commercial valuation of dynamite glycerin. The yield of nitroglycerin should be at least from 207-210 per cent. The quantity of nitroglycerin contained in the washings (recovered on the large scale by the so-called after-separation) is disregarded. The theoretical yield of nitroglycerin from glycerol is 246·7 per cent.

It is, of course, necessary to destroy the nitroglycerin. This is done best by spreading out a sufficient quantity of dry sawdust in not too thick a layer in an open space (say in the yard and not too near a building), and running the nitroglycerin out of a separating funnel on to it whilst the operator carries it along the sawdust, so as to distribute the nitroglycerin in a slender continuous trail, taking care that no pool is formed. By applying a lighted match to one end of the trail the nitroglycerin will burn away quickly. The waste acids should be destroyed in a similar manner; when they are brought into contact with sawdust a violent reaction sets in, but there is no danger if the nitroglycerin has been separated off carefully.

The **residues from the distillation of glycerin** are used in the manufacture of shoe-blacking. They contain large proportions of ash and polyglycerols. The proportion of glycerol is best determined by the acetin method.

3. CHEMICALLY PURE GLYCERIN

The distilled glycerins described under No. 2 still contain impurities which render them unfit for pharmaceutical purposes. Hence, they must be subjected to a second distillation. If the distillation is carried out with sufficient care, the distillates will yield, after concentration and treatment with char, the chemically pure glycerin of commerce.

At a time when the art of preparing chemically pure glycerin was not so far advanced as it is to-day, some chemically pure glycerin was manufactured by allowing glycerin to crystallise, and by removing the impurities in a centrifugal machine; this process has, however, been abandoned not only on account of its high cost, but also on account of the inferiority of the product as compared with the best brands of chemically pure glycerin, for it was found that the crystals were apt to occlude impurities.

Chemically pure glycerin is obtainable in commerce in various concentrations; hence we find on the market chemically pure glycerin of 1·24 specific gravity, chemically pure glycerin of 1·25 specific gravity, and chemically pure glycerin of 1·26 specific gravity.

The chemically pure glycerin of the highest specific gravity should approach as nearly as possible the chemical substance glycerol, the properties of which have been described, page 131.

Such glycerin is odourless, colourless, of a pure sweet taste, and as free from impurities as it is possible to prepare a substance on a large scale. The preparation demanded by the Pharmacopœia is the purest commercial article.

Provided the chemically pure substance satisfies the qualitative tests to be described below, the proportion of glycerol can be ascertained by merely determining the **specific gravity** of the sample.

The following tables contain the specific gravities of aqueous solutions of chemically pure glycerin, as determined by *Lenz*,[1] *Strohmer*,[2] *Gerlach*,[3] and *Nicol*.[4]

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[1] *Zeits. analyt. Chem.* 19, 302.

[2] *Monatshefte für Chemie*, 5, 61.

[3] *Chemische Industrie*, 7, 281.

[4] *Pharm. Journ. and Transact.* 1887, 297.

[TABLE

Specific Gravities of Aqueous Solutions of Chemically Pure Glycerin

Glycerol. Per cent.	LENZ.	STROHMER.	GERLACH.		NICOL.
	Spec. Grav. at 12°-14° C. Water at 12° C.=1.	Spec. Grav. at 17·5° C. Water at 17·5° C.=1.	Spec. Grav. at 15° C. Water at 15° C.=1.	Spec. Grav. at 20° C. Water at 20° C.=1.	Spec. Grav. at 20° C. Water at 20° C.=1.
100	1·2691	1·262	1·2653	1·2620	1·26348
99	1·2664	1·259	1·2628	1·2594	1·26091
98	1·2637	1·257	1·2602	1·2568	1·25832
97	1·2610	1·254	1·2577	1·2542	1·25572
96	1·2584	1·252	1·2552	1·2516	1·25312
95	1·2557	1·249	1·2526	1·2490	1·25052
94	1·2531	1·246	1·2501	1·2464	1·24790
93	1·2504	1·244	1·2476	1·2438	1·24526
92	1·2478	1·241	1·2451	1·2412	1·24259
91	1·2451	1·239	1·2425	1·2386	1·23990
90	1·2425	1·236	1·2400	1·2360	1·23720
89	1·2398	1·233	1·2373	1·2333	1·23449
88	1·2372	1·231	1·2346	1·2306	1·23178
87	1·2345	1·228	1·2319	1·2279	1·22907
86	1·2318	1·226	1·2292	1·2252	1·22636
85	1·2292	1·223	1·2265	1·2225	1·22365
84	1·2265	1·220	1·2238	1·2198	1·22094
83	1·2238	1·218	1·2211	1·2171	1·21823
82	1·2212	1·215	1·2184	1·2144	1·21552
81	1·2185	1·213	1·2157	1·2117	1·21281
80	1·2159	1·210	1·2130	1·2090	1·21010
79	1·2122	1·207	1·2102	1·2063	1·20739
78	1·2106	1·204	1·2074	1·2036	1·20468
77	1·2079	1·202	1·2046	1·2009	1·20197
76	1·2042	1·199	1·2018	1·1982	1·19925
75	1·2016	1·196	1·1990	1·1955	1·19653
74	1·1999	1·193	1·1962	1·1928	1·19381
73	1·1973	1·190	1·1934	1·1901	1·19109
72	1·1945	1·188	1·1906	1·1874	1·18837
71	1·1918	1·185	1·1878	1·1847	1·18565
70	1·1889	1·182	1·1850	1·1820	1·18293
69	1·1858	1·179	...	...	1·18020
68	1·1826	1·176	...	...	1·17747
67	1·1795	1·173	...	...	1·17474
66	1·1764	1·170	...	...	1·17201
65	1·1733	1·167	1·1711	1·1685	1·16928
64	1·1702	1·163	...	...	1·16654
63	1·1671	1·160	...	...	1·16380
62	1·1640	1·157	...	...	1·16107
61	1·1610	1·154	...	...	1·15834
60	1·1582	1·151	1·1570	1·1550	1·15561
59	1·1556	1·149	...	...	1·15288
58	1·1530	1·146	...	...	1·15015
57	1·1505	1·144	..	...	1·14742
56	1·1480	1·142	...	...	1·14469
55	1·1455	1·140	1·1430	1·1415	1·14196
54	1·1430	1·137	...	...	1·13923
53	1·1403	1·135	...	...	1·13650
52	1·1375	1·133	...	...	1·13377
51	1·1348	1·130	...	..	1·13104
50	1·1320	1·128	1·1290	1·1280	1·12831
45	1·1183	...	1·1155	1·1145	1·11469
40	1·1045	...	1·1020	1·1010	1·10118
35	1·0907	...	1·0885	1·0875	1·08786
30	1·0771	...	1·0750	1·0740	1·07469
25	1·0635	...	1·0620	1·0610	1·06166
20	1·0498	...	1·0490	1·0480	1·04884
15	1·0374	...	...	...	1·03622
10	1·0245	...	1·0245	1·0235	1·02391
5	1·0123	...	...	...	1·01184
0	1·0000	...	1·0000	1·0000	1·00000

The purity of the specimen of chemically pure glycerin used by *Lenz* had been ascertained by ultimate analysis. *Strohmer* employed crystallised glycerin freed from water by pressing repeatedly between folds of filter paper. *Gerlach* prepared his most concentrated glycerin by boiling down chemically pure glycerin of spec. grav. 1·220, until it reached a temperature at 290° C., at which the boiling point remained constant.

The specific gravities of aqueous solutions for each degree below 50 per cent are given in the tables pp. 1102, 1106, 1107.

Specific gravities found at temperatures other than those given in the table may be corrected by reference to the following table, due to *Gerlach*:—

Expansion of Aqueous Solutions of Glycerin. Volume at 0° *C.* = 10,000

Glycerol	Volume at 0° C.	Volume at 10° C.	Volume at 20° C.	Volume at 30° C.
Per cent.				
0	10,000	10,001·3	10,016·0	10,041·5
10	10,000	10,010	10,030	10,059
20	10.000	10,020	10,045	10,078
30	10,000	10,025	10,058	10,037
40	10,000	10,030	10,067	10,111
50	10,000	10,034	10,076	10,124
60	10,000	10,038	10,084	10,133
70	10,000	10,042	10,091	10,143
80	10,000	10,043	10,092	10,144
90	10,000	10,045	10,095	10,148
100	10,000	10,045	10,090	10,150

The numbers for intermediate temperatures are found by interpolation. For temperatures lying between 15° and 20° C. the specific gravity can be calculated from the numbers given by *Gerlach* (table p. 1102) by means of the following formula:—

$$s_t = s_1 + \frac{t-15}{5}(s_2 - s_1),$$

where

s_1 is the specific gravity of the glycerin at 15° C. Water at 15° C. = 1.
s_2 ,, ,, ,, 20° C. ,, 20° C. = 1.
s_t ,, ,, ,, t° C. ,, t° C. = 1.

A few of the numbers contained in the table p. 1102, have been controlled by ultimate analysis by *Morawski*.[1] His results show that *Lenz's* figures are, as a rule, a little too low, those of *Strohmer* a little too high, whereas *Gerlach's* and *Skalweit's* values agree both amongst themselves and with the results of elementary analysis.

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[1] *Chem. Zeit.* 13, 431. It may be added here that *Morawski's* method of determining the percentage of glycerol by means of lead oxide has been shown by Lewkowitsch (*Chem. Zeit.* 1889, 94. Cp. also *Chem. Anal. of Oils, Fats, and Waxes*, 2nd edition, 1898, p. 801), to yield unreliable results.

The specific gravity of the sample is taken by one of the methods described pp. 161-165. In the case of the most concentrated glycerin a slight complication arises, inasmuch as air bubbles easily become entangled, which rise only very slowly in the viscous liquid at the ordinary temperature. Thus if the hydrostatic balance be used, as is stipulated in many contracts (especially for dynamite glycerin, p. 1098), the determination may require hours, if the glycerin has not been poured into the cylinder carefully, allowing the substance to flow along the side of the vessel.

Hehner[1] recommends to fill a *Sprengel* tube with the glycerin at a higher temperature than the ordinary with the aid of the filter-pump, and then to immerse the tube in water of the normal temperature; for any other temperature a correction of 0·00058 for each degree centigrade must be made. By means of this factor *Richmond* has calculated the numbers given by *Lenz* to 15·5° C.:—

Glycerol.	Specific Gravity at 15·5° C.	Glycerol.	Specific Gravity at 15·5° C.
Per cent.		Per cent.	
100	1·2674	87	1·2327
99	1·2647	86	1·2301
98	1·2620	85	1·2274
97	1·2594	84	1·2248
96	1·2567	83	1·2222
95	1·2540	82	1·2196
94	1·2513	81	1·2169
93	1·2486	80	1·2143
92	1·2460	79	1·2117
91	1·2433	78	1·2090
90	1·2406	77	1·2064
89	1·2380	76	1·2037
88	1·2353	75	1·2011

I prefer the following method:—The sample is warmed in a closed bottle by immersing in warm water until the liquid has become perfectly free from air bubbles. The glycerin is then allowed to cool in the closed bottle, preferably to the normal temperature, and then carefully filled into an ordinary specific gravity bottle provided with a perforated stopper. If this has been pushed home, the minute drop of glycerin squeezed out is wiped off with a linen cloth and the bottle taken out of the water-bath. A number of comparative experiments, those made with the *Sprengel* tube being used as the standard, has proved that the specific gravities are correct to the fourth decimal if the weights are reduced to vacuum. Any complicated calculation is avoided by determining once for all the necessary corrections for the picnometer. Suppose p be the weight in air, then the corrected weight, P, will be

$$P = p + pR.$$

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[1] *Journ. Soc. Chem. Ind.* 1889, 8.

If brass weights are used, the correction, R, for the usual range of specific gravities is found from the following table :[1]—

Correction for Weights in Vacuo

Specific Gravity.	R.
1·00	0·00106
1·02	0·00103
1·04	0·00101
1·06	0·00099
1·08	0·00097
1·10	0·00095
1·15	0·00090
1·20	0·00086
1·25	0·00082
1·30	0·00078

Refractive Index.—The percentage of glycerol in a sample can be determined rapidly and with accuracy by means of the refractometer.

The numbers given in the following tables, due to *Lenz*, *Strohmer*, and *Skalweit*,[2] have been determined with *Abbe's* refractometer. According to *Lenz*, the several observations agree amongst each other to a few units of the fourth decimal, whilst the difference in the refractive indices corresponding to 1 per cent of glycerin amounts to 13·5 units of the fourth decimal. By reference to the tables, the percentage of glycerol in a sample can therefore be determined accurately to about 0·5 per cent.

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[1] Landolt, *Optisches Drehungsvermögen*, 1st ed., p. 131.

[2] *Repert. Anal. Chem.* 5, 18.

[Table

Specific Gravities and Refractive Indices of Aqueous Solutions of Chemically Pure Glycerin (Lenz)

Glycerol.	Sp. Gr. at 12°-14° C.	Ref. Ind. at 12·5°-12·8° C.	Glycerol.	Sp. Gr. at 12°-14° C.	Ref. Ind. at 12·5°-12·8° C.	Glycerol.	Sp. Gr. at 12°-14° C.	Ref. Ind. at 12·5°-12·8° C.
Per cent.			Per cent.			Per cent.		
100	1·2691	1·4758	66	1·1764	1·4249	32	1·0825	1·3745
99	1·2664	1·4744	65	1·1733	1·4231	31	1·0798	1·3732
98	1·2637	1·4729	64	1·1702	1·4213	30	1·0771	1·3719
97	1·2610	1·4715	63	1·1671	1·4195	29	1·0744	1·3706
96	1·2584	1·4700	62	1·1640	1·4176	28	1·0716	1·3692
95	1·2557	1·4686	61	1·1610	1·4158	27	1·0689	1·3679
94	1·2531	1·4671	60	1·1582	1·4140	26	1·0663	1·3666
93	1·2504	1·4657	59	1·1556	1·4126	25	1·0635	1·3652
92	1·2478	1·4642	58	1·1530	1·4114	24	1·0608	1·3639
91	1·2451	1·4628	57	1·1505	1·4102	23	1·0580	1·3626
90	1·2425	1·4613	56	1·1480	1·4091	22	1·0553	1·3612
89	1·2398	1·4598	55	1·1455	1·4079	21	1·0525	1·3599
88	1·2372	1·4584	54	1·1430	1·4065	20	1·0498	1·3585
87	1·2345	1·4569	53	1·1403	1·4051	19	1·0471	1·3572
86	1·2318	1·4555	52	1·1375	1·4036	18	1·0446	1·3559
85	1·2292	1·4540	51	1·1348	1·4022	17	1·0422	1·3546
84	1·2265	1·4525	50	1·1320	1·4007	16	1·0398	1·3533
83	1·2238	1·4511	49	1·1293	1·3993	15	1·0374	1·3520
82	1·2212	1·4496	48	1·1265	1·3979	14	1·0349	1·3507
81	1·2185	1·4482	47	1·1238	1·3964	13	1·0332	1·3494
80	1·2159	1·4467	46	1·1210	1·3950	12	1·0297	1·3480
79	1·2122	1·4453	45	1·1183	1·3935	11	1·0271	1·3467
78	1·2106	1·4438	44	1·1155	1·3921	10	1·0245	1·3454
77	1·2079	1·4424	43	1·1127	1·3906	9	1·0221	1·3442
76	1·2042	1·4409	42	1·1100	1·3890	8	1·0196	1·3430
75	1·2016	1·4395	41	1·1072	1·3875	7	1·0172	1·3417
74	1·1999	1·4380	40	1·1045	1·3860	6	1·0147	1·3405
73	1·1973	1·4366	39	1·1017	1·3844	5	1·0123	1·3392
72	1·1945	1·4352	38	1·0989	1·3829	4	1·0098	1·3380
71	1·1918	1·4337	37	1·0962	1·3813	3	1·0074	1·3367
70	1·1889	1·4321	36	1·0934	1·3798	2	1·0049	1·3355
69	1·1858	1·4304	35	1·0907	1·3785	1	1·0025	1·3342
68	1·1826	1·4286	34	1·0880	1·3772			
67	1·1795	1·4267	33	1·0852	1·3758			

[TABLE

Specific Gravities and Refractive Indices of Aqueous Solutions of Chemically Pure Glycerin (Strohmer)

Glycerol. Per cent.	Sp. Gr. at 17·5° C.	Ref. Ind. at 17·5° C.	Glycerol. Per cent.	Sp. Gr. at 17·5° C.	Ref. Ind. at 17·5° C.	Glycerol. Per cent.	Sp. Gr. at 17·5° C.	Ref. Ind. at 17·5° C.
100	1·262	1·4727	83	1·218	1·4478	66	1·170	1·4206
99	1·259	1·4710	82	1·215	1·4461	65	1·167	1·4189
98	1·257	1·4698	81	1·213	1·4449	64	1·163	1·4167
97	1·254	1·4681	80	1·210	1·4432	63	1·160	1·4150
96	1·252	1·4670	79	1·207	1·4415	62	1·157	1·4133
95	1·249	1·4653	78	1·204	1·4398	61	1·154	1·4116
94	1·246	1·4636	77	1·202	1·4387	60	1·151	1·4099
93	1·244	1·4625	76	1·199	1·4370	59	1·149	1·4087
92	1·241	1·4608	75	1·196	1·4353	58	1·146	1·4070
91	1·239	1·4596	74	1·193	1·4336	57	1·144	1·4059
90	1·236	1·4579	73	1·190	1·4319	56	1·142	1·4048
89	1·233	1·4563	72	1·188	1·4308	55	1·140	1·4036
88	1·231	1·4551	71	1·185	1·4291	54	1·137	1·4019
87	1·228	1·4534	70	1·182	1·4274	53	1·135	1·4008
86	1·226	1·4523	69	1·179	1·4257	52	1·133	1·3997
85	1·223	1·4506	68	1·176	1·4240	51	1·130	1·3980
84	1·220	1·4489	67	1·173	1·4223	50	1·128	1·3969

Specific Gravities and Refractive Indices of Aqueous Solutions of Chemically Pure Glycerin (Skalweit)

Glycerol. Per cent.	Sp. Gr. at 15° C.	$n_{[D]}$ [1] at 15° C.	Glycerol. Per cent.	Sp. Gr. at 15° C.	$n_{[D]}$ at 15° C.	Glycerol. Per cent.	Sp. Gr. at 15° C.	$n_{[D]}$ at 15° C.
0	1·0000	1·3330	34	1·0858	1·3771	68	1·1799	1·4265
1	1·0024	1·3342	35	1·0885	1·3785	69	1·1827	1·4280
2	1·0048	1·3354	36	1·0912	1·3799	70	1·1855	1·4295
3	1·0072	1·3366	37	1·0939	1·3813	71	1·1882	1·4309
4	1·0096	1·3378	38	1·0966	1·3827	72	1·1909	1·4324
5	1·0120	1·3390	39	1·0993	1·3840	73	1·1936	1·4339
6	1·0144	1·3402	40	1·1020	1·3854	74	1·1963	1·4354
7	1·0168	1·3414	41	1·1047	1·3868	75	1·1990	1·4369
8	1·0192	1·3426	42	1·1074	1·3882	76	1·2017	1·4384
9	1·0216	1·3439	43	1·1101	1·3896	77	1·2044	1·4399
10	1·0240	1·3452	44	1·1128	1·3910	78	1·2071	1·4414
11	1·0265	1·3464	45	1·1155	1·3924	79	1·2098	1·4429
12	1·0290	1·3477	46	1·1182	1·3938	80	1·2125	1·4444
13	1·0315	1·3490	47	1·1209	1·3952	81	1·2152	1·4460
14	1·0340	1·3503	48	1·1236	1·3966	82	1·2179	1·4475
15	1·0365	1·3516	49	1·1263	1·3981	83	1·2206	1·4490
16	1·0390	1·3529	50	1·1290	1·3996	84	1·2233	1·4505
17	1·0415	1·3542	51	1·1318	1·4010	85	1·2260	1·4520
18	1·0440	1·3555	52	1·1346	1·4024	86	1·2287	1·4535
19	1·0465	1·3568	53	1·1374	1·4039	87	1·2314	1·4550
20	1·0490	1·3581	54	1·1402	1·4054	88	1·2341	1·4565
21	1·0516	1·3594	55	1·1430	1·4069	89	1·2368	1·4580
22	1·0542	1·3607	56	1·1458	1·4084	90	1·2395	1·4595
23	1·0568	1·3620	57	1·1486	1·4099	91	1·2421	1·4610
24	1·0594	1·3633	58	1·1514	1·4104	92	1·2447	1·4625
25	1·0620	1·3647	59	1·1542	1·4129	93	1·2473	1·4640
26	1·0646	1·3660	60	1·1570	1·4144	94	1·2499	1·4655
27	1·0672	1·3674	61	1·1599	1·4160	95	1·2525	1·4670
28	1·0698	1·3687	62	1·1628	1·4175	96	1·2550	1·4684
29	1·0724	1·3701	63	1·1657	1·4190	97	1·2575	1·4698
30	1·0750	1·3715	64	1·1686	1·4205	98	1·2600	1·4712
31	1·0777	1·3729	65	1·1715	1·4220	99	1·2625	1·4728
32	1·0804	1·3743	66	1·1713	1·4235	100	1·2650	1·4742
33	1·0831	1·3757	67	1·1771	1·4250			

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[1] $n_{[D]}$ is the refractive index for the sodium line D.

It must, however, be distinctly understood that the numbers given for refractive indices hold good only for the stated temperatures. The variations due to change of temperature may be gathered from the following table :—

Specific Gravity.	Variation of Refractive Index for 1° C.	Observer.
1·25350	0·00032	Listing
1·24049	0·00025	Van der Willigen
1·19286	0·00023	,,
1·16270	0·00022	,,
1·11463	0·00021	,,

The variation in the case of pure water is 0·00008 for 1° C.

With a view to eliminating slight errors due to the adjustment of the instrument, *Lenz* recommends to take, immediately after the sample has been examined, the refractive index of water, of course at the same temperature. Thus the numbers given in the following table were obtained :—

Difference between Refractive Indices of Aqueous Solutions of Chemically Pure Glycerin and Pure Water (*Lenz*)

Glycerol	$n_{[D]}$ Glycerol − $n_{[D]}$ Water.	Glycerol	$n_{[D]}$ Glycerol − $n_{[D]}$ Water.	Glycerol	$n_{[D]}$ Glycerol − $n_{[D]}$ Water.	Glycerol	$n_{[D]}$ Glycerol − $n_{[D]}$ Water.
Per cent.		Per cent.		Per cent.		Per cent.	
100	0·1424	74	0·1046	48	0·0645	22	0·0288
99	0·1410	73	0·1032	47	0·0630	21	0·0275
98	0·1395	72	0·1018	46	0·0616	20	0·0261
97	0·1381	71	0·1003	45	0·0601	19	0·0238
96	0·1366	70	0·0987	44	0·0587	18	0·0225
95	0·1352	69	0·0970	43	0·0572	17	0·0212
94	0·1337	68	0·0952	42	0·0556	16	0·0199
93	0·1323	67	0·0933	41	0·0541	15	0·0186
92	0·1308	66	0·0915	40	0·0526	14	0·0173
91	0·1294	65	0·0897	39	0·0510	13	0·0160
90	0·1279	64	0·0889	38	0·0495	12	0·0146
89	0·1264	63	0·0861	37	0·0479	11	0·0133
88	0·1250	62	0·0842	36	0·0464	10	0·0120
87	0·1235	61	0·0824	35	0·0451	9	0·0108
86	0·1221	60	0·0806	34	0·0438	8	0·0096
85	0·1206	59	0·0792	33	0·0424	7	0·0083
84	0·1191	58	0·0780	32	0·0411	6	0·0071
83	0·1177	57	0·0768	31	0·0398	5	0·0058
82	0·1162	56	0·0757	30	0·0385	4	0·0046
81	0·1148	55	0·0745	29	0·0372	3	0·0033
80	0·1133	54	0·0731	28	0·0358	2	0·0021
79	0·1119	53	0·0717	27	0·0345	1	0·0008
78	0·1104	52	0·0702	26	0·0332	0	0·0000
77	0·1090	51	0·0688	25	0·0318		
76	0·1075	50	0·0663	24	0·0315		
75	0·1061	49	0·0659	23	0·0302		

In the case of dilute solutions of chemically pure glycerin, the specific gravity and refractive index give the percentage less accurately than the methods described, pp. 281-288.

The oxidation methods should yield theoretical results if the glycerin be really chemically pure, but in case minute quantities of organic impurities have remained in the product, the percentage will be found too high. This is shown by a comparison of the following two analyses (*Lewkowitsch* [1]).

Comparison of the Acetin and Bichromate Methods

	Acetin Method.	Bichromate Method.
Chemically pure glycerin, specific gravity 1·2618.	99·04 ; 99·17	101·00 ; 101·9

In case the acetin method be resorted to, about 1 gram of the substance is taken, and the excess of acetic anhydride must be somewhat larger than usual so as to ensure complete esterification.

Ash.—Theoretically, the proportion of ash should be *nil*, but since the last traces of metals cannot be removed from a product manufactured on a large scale, minute traces of ash will always be found. The table given (p. 1111) shows the amount of ash ascertained by me in a number of commercial chemically pure glycerins. These numbers will afford guidance in judging as to whether in a given case the permissible maximum has been exceeded.

The ash may contain traces of sodium chloride. Lime and lead are not met with at present in chemically pure glycerins. The ash will chiefly contain copper or iron. The presence of iron can be ascertained by treating the glycerin with a dilute solution of tannin.

Organic impurities.[2]—These impurities are due to faulty manufacture, and may either consist of *acroleïn* and volatile fatty acids, as *butyric acid*, or of substances having a higher boiling point than glycerol itself. The latter substances may be comprised under the name *polyglycerols.*

A rapid "practical" test for volatile fatty acids is to spread a few drops of the sample on the back of the hand, and rub it gently into the skin. No smell of acroleïn or butyric acid should be then noticeable. A more reliable method is to mix the sample with alcohol and concentrated sulphuric acid, and heat over a flame. In the presence of butyric acid the characteristic smell of pine apples, due to ethyl butyrate, will be noticed.

Acroleïn (as also other reducing substances) is best detected by adding a few drops of a silver nitrate solution to the aqueous solution

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[1] *Analyst*, 1903, 105.

[2] Lewkowitsch, *Year-Book of Pharmacy*, 1890, 382.

of glycerin. No blackening or browning should appear after standing for twenty-four hours at the ordinary temperature.

The German Pharmacopœia, edit. iii., prescribed the silver test in the following form:—Heat 1 c.c. of glycerin with 1 c.c. of ammonia to boiling, and add three drops of silver nitrate solution. No discolouration should be noticeable within five minutes. This test was originally intended to detect presence of arsenic, but is absolutely unreliable for this purpose. It is also worthless for the detection of other impurities, as so much depends on the mode of operating, that on the one hand an impure glycerin, one even that has not been distilled, may conform to the test, whereas on the other hand a pure glycerin is liable to be rejected. At the temperature of boiling water a mixture of glycerol and silver nitrate *does* become reduced at once on addition of ammonia (p. 138). If the enormous excess of ammonia is mixed with glycerol, according to the directions of the Pharmacopœia, ebullition of the liquid may take place before the temperature of 100° C. is reached, and in that case the silver nitrate subsequently added will not be reduced.[1]

This method should therefore be rejected.

From these remarks it will be understood that the silver nitrate test can be made far more sensitive if, instead of neutral silver nitrate, an ammoniacal silver nitrate solution be used in the cold. Even the minutest traces of organic impurities, such as acroleïn, may be thus detected.

Acroleïn may be also detected by one of the tests described, p. 136.

Sugar.—Adulteration of glycerin with sugar (cane sugar or glucose) does occur when glycerin is high in price. The presence of sugars is detected by polarimetric examination.

Polyglycerols[2] are detected and determined by allowing an accurately weighed quantity of the sample to evaporate gently at 160° C. Care should be taken not to heat too rapidly, otherwise even the purest glycerin may become polymerised with the production of the very substance that is to be detected. From the weight of the residue the weight of ash, subsequently found on incineration, must be deducted. The difference (the "organic residue") is a fair indication of the care with which the glycerin has been manufactured.

The following table gives the "organic residue" and ash of a number of "chemically pure glycerins" examined in my laboratory,[2] and arranged according to the amount of organic residue they contain:—

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[1] It may be added here that the Pharmacopœia test has met with a strenuous objection on the part of a number of German glycerin manufacturers, who declared in a circular that they could not supply an article satisfying the Pharmacopœia test.

[2] Lewkowitsch, *Year-Book of Pharmacy*, 1890, 382.

[TABLE

Organic Residue and Ash in Commercial Chemically Pure Glycerins (Lewkowitsch)

No.	Residue at 160° C.	Ash.	Organic Residue.
	Per cent.	Per cent.	Per cent.
1	0·03033	0·00603	0·0243
2	0·0276	0·00300	0·0246
3	0·0377	0·005	0·0327
4	0·0498	0·0138	0·0360
5	0·0452	0·0081	0·0371
6	0·0509	0·0066	0·0443
7	0·0656	0·0139	0·0517
8	0·0748	0·0140	0·0738
9	0·0905	0·0154	0·0751
10	0·1047	0·0190	0·0857
11	0·1236	0·0305	0·0931
12	0·1621	0·0183	0·1438
13	0·8060	0·2090	0·5970

Rules for the valuation of commercial chemically pure glycerins may be derived from this table. The first six samples certainly deserve the name of chemically pure glycerin, the following four samples represent lower qualities unfit for pharmaceutical purposes, whereas the last two samples are merely glycerins refined by distillation; the last sample would be rejected as unsuitable even by dynamite makers.

Sample No. 2 represents chemically pure glycerin manufactured by the writer on a large scale from soap-lye glycerin.

One of the most important tests in the examination of chemically pure glycerin is the test for **Arsenic.**

This metal should be wholly absent. It should be borne in mind that once arsenic has found its way into glycerin, it cannot be removed by the usual processes of refining,[1] as glycyl arsenite, $AsO_3(C_3H_5)$, the substance formed when arsenious acid is dissolved in glycerin, distils over with the latter (cp. p. 135). Hence many commercial brands are contaminated with arsenic, some to such an extent that they are decidedly harmful when used for medicinal preparations, or are otherwise taken inwardly.

A rapid and extremely sensitive test for arsenic is *Gutzeit's* test :—

Place 2 c.c. of the sample in a high test-tube, add some zinc, free from arsenic, and a few c.c. of pure dilute sulphuric acid. The test-tube is then covered with a tightly fitting cap of filtering paper, two or three layers thick, the innermost layer having been previously moistened, by the aid of a glass rod, with a 50 per cent solution of silver nitrate. In presence of arsenic arseniuretted hydrogen is given off. After ten minutes' standing the paper cap is taken off and

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[1] Lewkowitsch, *Year-Book of Pharmacy*, 1890, 380.

examined. No deep yellow stain must be noticeable on the inner fold, a slight yellowish colouration only being permissible. This test is so extremely sensitive that it is absolutely necessary to make side by side with it a blank test, using the same reagents. The silver nitrate test is almost too delicate (although there are commercial glycerins which will not show any colouration after ten minutes) and has therefore been replaced by less rigorous tests. If in *Gutzeit's* test a concentrated solution of mercury bichloride is substituted for silver nitrate, a glycerin may be considered as practically free from arsenic should no yellow colouration appear after ten minutes. In case mercury bichloride be used, hydrochloric acid may be employed instead of sulphuric acid. On testing with silver nitrate, hydrochloric acid should be avoided, as hydrochloric acid gas may be given off if the liquid becomes too hot.[1]

It should, however, be noted that sulphuretted hydrogen, evolved if sulphides be present, also produces a yellow stain. In order to exclude errors, sulphides must be oxidised to sulphates. I test for presence of sulphides by proceeding as in *Gutzeit's* test, but substituting a paper cap moistened with lead acetate instead of silver nitrate; a black stain points to sulphides.

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[1] With regard to the use of the Marsh apparatus, cp. "Detection and Determination of Arsenic." Reprinted from the *Journal of the Society of Chemical Industry.* Eyre and Spottiswoode, London, 1901.

CHAPTER XVI

TECHNOLOGY OF WASTE FATS

1. Greases

In the wider sense of the term, kitchen-grease, ship's-grease, skin-grease, slaughter-house grease, and similar fats fall under the head of "Waste Fats." These greases must be looked upon as varieties of tallow, horse fat, etc. It may, therefore, suffice here to summarise the analyses of a few typical greases examined in my laboratory.

Analyses of Greases (Lewkowitsch.)

	Ash.	Free Fatty Acids.	Neutral Fat.	Unsaponifiable.
	Per cent.	Per cent.	Per cent.	Per cent.
White skin grease	...	3·6	96·0	...
Light skin grease	0·077	12·3	86·0	...
Brown skin grease	0·03	13·9	77·2	9·1
"Animal grease"	0·96	31·4	65·7	2·8
Dark skin grease[1]	1·78	22·7	60·7	...
,, ,, ...	...	24·0	64·0	...

"Bone fat," "bone grease," may also be looked upon as a waste fat. Its manufacture and properties have been described already in Chapter XIV.

These materials are used as substitutes of tallow, etc., for various technical purposes (lubricating greases). When prices of oils and fats are high, they enter to a somewhat notable proportion into the composition of low class soaps, and are even employed in candle making. "Fish stearine" may be taken as an example.

The "fish stearine" of commerce is of varying composition, and represents either the solid glycerides from fish oils, cod liver oil, seal oil, whale oil (cp. Chap. XV. under the heads of these oils) or a mixture of all these "stearines." Their commercial uses have been

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[1] The grease extracted from tanned skins must not be confounded with skin grease. The composition of the grease from tanned leather has not been thoroughly examined yet; it contains considerable quantities of unsaponifiable matter, and has the property of taking up a considerable quantity of water.—(J. T. Wood.)

pointed out already. "Fish stearine" was proposed as a candle material by *Hajek*.[1] Although this waste fat is at present of no practical importance to the candle-maker, the results obtained by *Hajek* are recorded here, as they may deserve attention in case fats reach again the high prices of the last few years. The examination of six specimens of "fish stearine" gave the following numbers (*Hajek*):—

Fish Stearine.	Fat.					Fatty Acids.	
	Impurities.[2]	Melting Point.	Iodine Value.	Acid Value.	Fatty Acids.	Solidifying Point.	Melting Point.
No.	Per cent.	°C.	Per cent.		Per cent.	°C.	°C.
1	4·0	43·5	42·3	16·9	90·2	...	44·5
2	5·6	40·0	44·0	20·9	91·0	...	38·0
3	5·7	46·5	41·0	30·0	90·0	43·0	45·0
4	5·2	...	...	20·0	91·0	42·5	44·75
5	6·0	44·5	...	40·0	95·5	41·75	43·50
6	15·0	46·5	...	...	80·8	...	45·0

A somewhat large quantity of washed and dried "fish stearine" containing 7 per cent "impurities" was autoclaved with 2·5 per cent of lime at a pressure of eight atmospheres during seven hours, and is stated by *Hajek* to have yielded 94 per cent of crude fatty acids, containing 3 per cent of unsaponifiable matter. The yield of glycerin of 28° Bé is stated to have been 7·3 per cent of the autoclaved mass. The fatty acids were then distilled; nine samples taken at intervals of two hours showed the following characteristics:—

Sample.	Colour.	Appearance.	Solidifying Point.	Melting Point.
No.			°C.	° C.
1	Green	Forming scales	46	48·75
2	,,	,,	47·1	49·2
3	White	Amorphous, containing some crystals	47·5	49·5
4	,,		47·75	50·0
5	,,		48·50	50·25
6	Greyish white		48·75	50·75
7	Grey		47·50	49·50
8	,,		42·50	44·50
9	,,	Viscous	...	36·00

The total yield obtained on distillation is stated as follows:—

	Per cent.
Fatty acids	95·77
Stearine-Pitch (Goudron)	3·50
Loss (by difference)	0·73
	100·00

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[1] *Augsburger Seifensieder Zeit.* 1903, 580.

[2] The impurities include all non-fatty (especially gelatin-like) substances.

Laboratory experiments carried out with a view to increasing the yield of candle material by acidifying the fatty acids before distillation (cp. Mixed Process, Chap. XV.) did not lead to satisfactory results. The final result of the large scale experiment is stated in the following table:—

	Per cent.
"Stearine" (candle material)	53·10
Oleine	36·90
Stearine Pitch (Goudron)	3·29
Glycerin, 28° Bé	7·00
	100·29

2. Cotton Seed Foots

In the refining of cotton seed oil by means of caustic soda (p. 525) a precipitate is obtained, consisting of a mixture of cotton seed oil soap, colouring and resinous matters, known in this country under the trade term "mucilage."

The American cotton seed oil foots are of comparatively light colour, as the seed is pressed whilst still fresh; these "foots" can therefore be used for soap-making. Large quantities of this material are imported from America and sold as a "milling" soap for the cheapest class of goods.

The Egyptian seed, crushed chiefly in this country, usually "heats" during the voyage and on storing; in consequence of the changes which the seed has undergone, the crude cotton seed oil has a very dark colour, and the foots obtained from it are almost black. The considerable quantity of soap and oil contained in this "mucilage" are recovered by treatment with a mineral acid; the separated fatty mass is then distilled by means of superheated steam, in the same manner as the distillation of the fatty acids is carried out (Chap. XV. p. 1021).

The distillate thus obtained consists chiefly of free fatty acids, and is worked up in the same manner as the distilled fatty acids of the candle-works. Thus "oleine" and "stearine" are obtained. The latter is frequently termed "cotton seed stearine," and must not be confounded with the true cotton seed stearine (or vegetable margarine) described p. 526. The still residue is cotton stearine pitch.

The "oleine" and "stearine" are put to the same uses as the candle-works products. Their examination is carried out on the same lines. Thus a sample of stearine tested in my laboratory had a solidifying point 45·6° C., and contained 5·2 per cent of unsaponifiable matter. The iodine value of the sample was 54·9.

3. Fuller's Grease—"Seek Oil"

French—*Graisse de foule.* German—*Walkfett.*

Fuller's grease is the fatty substance recovered from the soap suds which have served for scouring silk, woollen, or cotton (dyed

Turkey-red) goods by acidifying with a mineral acid. The fatty mass thrown up by the acid (known in Yorkshire under the name "magma" or "seek," also "sake"; therefore "seek oil" means fuller's grease) is put into bags, and subjected to pressure whilst hot, when the dirt (fibres, etc.), remain behind, whereas the expressed fatty matter is collected in tanks below the press.

According to the soap used for scouring the goods (and, in the case of grease from woollen mills, according to the quality of wool oil that has been used in the spinning of the wool), the quality of fuller's grease will vary. Hence the uses to which fuller's grease is applied also vary. Thus, the suds from silk or best woollen goods, for which olive oil soap has been used, will yield almost pure fatty acids, which may be converted into soap without further purification, whereas the suds from the lowest union goods contain considerable quantities of mineral oil or other hydrocarbons and dirt. Therefore the crude grease must be purified by distillation. The distilled "oleine" so obtained is used as wool oil (p. 959). An intermediate quality of fuller's grease is prepared by purifying the crude material by filtration. This material is likely to contain mineral acid.

The commercial examination of fuller's grease is identical with that of wool oils (p. 954).

4. Black (recovered) Oil

This oil is expressed or extracted from the greasy waste of woollen mills, collected from beneath the carding and scribbling machines. Its composition should be almost identical with that of the oil employed for oiling the wool for the carding process. This oil may comprise, therefore, all gradations from a rancid olive oil, through oleic acid, down to the lowest class wool oils, containing more than 50 per cent of unsaponifiable matter.

5. Wool Grease, "Recovered Grease" "Brown Grease,"[1]

The occurrence and preparation of wool grease has been described already in Chapter XIV. p. 877. The composition of wool grease varies considerably, as has also been pointed out above.

A special kind of wool grease is the grease recovered from the Yorkshire woollen mills, and known as "Yorkshire grease." This is prepared by collecting the soap suds from the woollen mills, and acidifying them with mineral acid, when the wool grease and the fatty acids from the soap used in scouring, rise to the top. The fatty matter is collected by skimming off, and expressed in a hydraulic press at a high temperature, so as to remove the fibres, dirt, etc.,

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[1] In the United States this grease is known commercially as "dégras."

that are occluded by the fatty matter. The composition of a genuine grease of this kind, free from glycerides, mineral oil, and freed from ash, was examined in my laboratory with the following results :[1]—

	Per cent.
Volatile acids	1·28
Insoluble free fatty acids	20·22
Combined fatty acids	48·47
Alcohols	36·47

The proportion of *volatile acids* appears to be due to secondary reactions. *A. and P. Buisine*[2] point to fermented wool scourer's suds as a rich source of volatile fatty acids, from acetic acid up to caproic acid.

The free fatty acids partly occur naturally in wool grease,[3] and are partly due to decomposition of the waste soap suds.

The combined fatty acids form with the bulk of the *alcohols* neutral esters (wax). In the example given above the proportion of neutral esters amounted to 72·31 per cent (cp. p. 412).

The alcohols were partly present as esters combined with fatty acids to form 72·31 per cent of wax, the remainder being free alcohols. In the given example their amount was 6·21 per cent (cp. p. 412).

The methods adopted in the analysis of this grease have been fully described p. 409.

By the process of recovery outlined above a considerable amount of fatty acids is lost. Hence a number of patents have been taken for extracting raw wool on a large scale with volatile solvents. A process for the recovery of wool grease without the use of mineral acids or solvents has been patented by *Smith* and *Leach*. The wash waters are concentrated in multiple vacuum apparatus, and when the desired concentration is reached they are passed through a centrifugal machine, where the soap liquor and sand are removed, the neutral wool grease remaining behind.

The efforts of several inventors (*Jaffé* and *Darmstädter*, *Ekenberg* and *Montén*) have been directed to the separation of wool fat into several fractions. Thus *Ekenberg* and *Montén* prepared three fractions termed by them "Cholaïn," "Cholepalmin," and "Cholecerin." Their melting points are the following :—

	Melting Point. °C.
Cholaïn	25-29
Cholepalmin	37-38
Cholecerin	49-55

A considerable portion of wool grease is freed from fatty acids on the large scale, and worked up into neutral wool wax. The crude

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[1] Lewkowitsch, *Journ. Soc. Chem. Ind.* 1892, 134.

[2] *Compt. rend.* (1897) 125, 777.

[3] Schulze, *Berichte*, 1872, 1076 ; 1873, 251 ; 1874, 571.

wool grease is used as a lubricant, with or without admixture of mineral oils (see "Wool Oils," p. 959), further as a dégras substitute (see p. 1129), and as a stuffing grease (see p. 1129).

The bulk of wool grease is, however, distilled in this country, yielding "distilled greases."

DISTILLED GREASE

When the "recovered grease" is subjected to distillation with superheated steam the compound esters are broken up, the free fatty acids simultaneously undergoing partial decomposition. A light oil, consisting of hydrocarbons, is obtained first; then follow heavier distillates, which are separated into a liquid and a solid portion by cooling and allowing to crystallise. These fractions are treated much in the same way as the distilled fatty acids in candle works, so that the following products are finally obtained: "oleine," chiefly used as wool oil (p. 959), and "stearine," employed as a "sizing tallow" or "stuffing grease," and as inferior material for the candle and soap industries.

The changes the "recovered grease" undergoes in the distillation consist, according to *Lewkowitsch*,[1] in the first instance, in the breaking up of the compound esters into fatty acids and hydrocarbons, the latter being formed in consequence of the fatty acids assimilating all the available oxygen in the molecule. This is illustrated by the following equation:—

$$\underset{\text{Cetyl palmitate.}}{C_{15}H_{31}CO\,.\,O\,.\,C_{16}H_{33}} = \underset{\text{Palmitic acid.}}{C_{15}H_{31}CO\,.\,OH} + \underset{\text{Cetene.}}{C_{16}H_{32}}.$$

A portion of the neutral esters is carried away undecomposed by the current of steam, and is found as such in the "distilled grease."

The free alcohols in the "recovered grease" partly distil over as such, another portion is broken up into hydrocarbons with loss of water; thus cholesterol, when subjected to distillation, is known to yield hydrocarbons.

Part of the fatty acids in their turn, especially those easily undergoing dehydration, are also converted into hydrocarbons.

The examination of the distilled greases embraces the determination of *free fatty acids*, *neutral esters* (*waxes*), and *unsaponifiable substances*. The latter consist chiefly of hydrocarbons, which have been looked upon frequently as mineral oil (cp. "Wool Oils"). The nature of these hydrocarbons is but very imperfectly known; being derivatives of cholesterol, they exhibit optical activity.

The methods applicable to the complete examination of distilled grease have been fully described in Chap. XI. p. 413.

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[1] *Journ. Soc. Chem. Ind.* 1892, 142.

The commercial analysis of **distilled grease oleine** for oiling wool has been described under "Wool Oils," p. 955.

Distilled grease stearine is a hard, whitish, solid substance, differing in its appearance from commercial stearic acid by the absence of crystalline structure. This stearine is easily identified by the strong isocholesterol reaction (p. 141) and its high iodine value, due to presence of isooleic acid. It consists chiefly of free acid, the bulk of the hydrocarbons having been removed by pressing. In commercial analysis the melting and solidifying points of the stearine, the "saponifiable," and the "unsaponifiable" are required.

The "saponifiable" is ascertained by boiling an accurately weighed quantity with standard alcoholic potash, as described under "saponification value." Each c.c. of normal alkali is taken as corresponding to 0·284 grm. of stearic acid. (The small quantity of neutral esters (if any) in the stearine is thus calculated as stearic acid.) The unsaponifiable matter is determined in the manner described above (p. 293); it is most convenient to use for this test that quantity which has served for the determination of the "saponifiable."

The following table gives a few analyses of "distilled grease stearine." The free acid has been calculated as stearic acid :—

Solidifying Point.	Melting Point.	Specific Gravity.		Water.	Free Acid.	Neutral Ethers.	Unsaponifiable.	Iodine Value.	Observer.
°C.	°C.	At 15·5° C.	At 98° C.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	
45	48	0·9193	0·836	0·6	88·6	2·11	0·49	...	Hurst
53·5	57	0·9044	...	1·48	76·3	7·7	0·4	...	,,
...	...	...	...	2·85	72·13	...	3·12	...	,,
41·5	...	...	...	...	98·9	...	...	33·7	Lewkowitsch
...	...	...	...	...	...		7·2	...	,,

The residue left in the stills, **wool fat pitch** (goudron), is used as a lubricant for hot neck rollers.

5. SOD OIL—DÉGRAS[1]

French—*Dégras.* German—*Gerberfett, Lederfett, Weissbrühe, Dégras.*

Sod oil or dégras[2] is the waste fat obtained in the chamoising process, and is used for currying purposes, *i.e.* dressing bark-tanned leather.

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[1] Jean, *Moniteur scientifique*, 15, 1889. Eitner, *Der Gerber*, 1890, 85. Simand, *Der Gerber*, 1890, 243 ; 254 ; 266 ; 279. Jahoda, *Zeit. angew. Chem.* 1891, 325. Fahrion, *Journ. Soc. Chem. Ind.* 1891, 557 ; 1013 ; 1893, 937. Ruhsam, *Journ. Soc. Chem. Ind.* 1892, 639. Weiss, *Journ. Soc. Chem. Ind.* 1893, 937. Eitner, *Der Gerber*, 1893, 257. Schmitz-Dumont, *Dingl. Polyt. Journ.* 1895, 296, Nos. 9-11 ; *Journ. Soc. Chem. Ind.* 1895, 815 ; 829. Tortelli, *Annali del Lab. Chim. Centr. delle Gabelle*, 1897, 184.

[2] It should be noted that in the United States "dégras" denotes the recovered grease from wool-scouring works.

The skins which are to be converted into chamois leather are first limed, the hair is then removed by the aid of a blunt dressing knife, and the unhaired hides placed in a "sour bath," made of refuse malt and bran, in which they "swell" in consequence of an acid fermentation (enzymes or oxydases, or *Bacterium erodiens*[1]), setting in. The skins are next stretched and well rubbed with whale or cod liver oil[2]—in the United States menhaden oil—and worked in a fulling machine, "stocks," so as to become thoroughly saturated with oil. Then the skins are taken out and exposed to the air. The same process of rubbing with oil and stamping in the stocks is repeated until enough oil has been absorbed, and the skins appear quite dry. In consequence of the exposure to the air, a portion of the oil has been somewhat changed, and has entered into "combination" with the fibre, another portion being only mechanically enclosed within the pores of the skin. The "combined oil" is that portion of altered fatty matter which cannot be extracted by carbon bisulphide.[3] In order to render the "combination" of the oil with the fibre more rapid, a fermentation attended with elevation of temperature is brought about by heaping the skins together in a warm room, and covering them carefully with canvas so as to keep the generated heat in the heap. Overheating, however, must be prevented by occasional turning over the pile so as to cool the skins. The oxidation of the oil is completed when the skins have acquired the yellow colour of chamois leather. About 50 per cent of the oil is then found to be left in the "uncombined" state, and is removed by one of the two following methods:—

English and German Method.—If no oil can be obtained by pressing or wringing, the excess must be removed from the skins by washing with alkaline lyes. The emulsion thus obtained is similar to a wool grease emulsion; like the latter it is acidified with sulphuric acid and the fatty matter is skimmed off. This fatty substance forms the *sod oil* of commerce.

This sod oil, in contradistinction to dégras, contains a considerable amount of water, soap, and impurities, such as hide fragments, etc. The sod oil is frequently dehydrated[4] by heating in a jacketed pan when the water is either evaporated off or settles out at the bottom of the pan. Such oil is, however, according to *Procter*,[5] no suitable substitute for the genuine dégras prepared by the French method.

According to *Procter*,[6] many English manufacturers have adopted the French process, so that their product does not differ from French moëllon. As much of the value of the sod oil depends on the state of emulsion in which it is kept by the water, it is a mistake to "evaporate" such sod oils.

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[1] Delbrück, *Zeit. ang. Chemie*, 1902, 694.

[2] With regard to a method of examining cod liver oils for tanning purposes, cp. Trotman and Peters, *Journ. Soc. Chem. Ind.* 1902, 694.

[3] Cp. v. Schroeder and Paessler, *Journ. Soc. Chem. Ind.* 1895, 759.

[4] *Leather Industries Laboratory Book*, 1898, 204.

[5] *Ibid.*

[6] *Ibid.*

French Method.—The skins are stocked, aired, and fermented for a shorter period than by the English or German process, so that a large proportion of the oil can be obtained from the skins by steeping them in warm water and wringing or pressing in hydraulic presses. The oil thus obtained is called "première torse," *moëllon*. The oil still retained by the skins is recovered by washing with alkali, as in the English and German method, and is usually added to the moëllon.

Whereas genuine *moëllon* consists only of expressed oil, a second quality termed "secunda dégras," or shortly "dégras," is prepared by mixing genuine moëllon with blubber oils or solid fats (such as tallow, palm nut oil, etc.). This product is still included amongst better qualities of dégras. In fact, according to *Procter*, pure moëllon is never sold as such, but always mixed with tallow and untreated oils; these admixtures cannot, therefore, be regarded as adulterants.

Numerous "substitutes" of dégras, or artificial dégras ("corroïne"), occur in commerce, consisting of largely adulterated dégras, or of more or less judiciously prepared mixtures of cod, whale, menhaden, sardine, Japan fish oils, blown blubber oils,[1] tallow,[2] rosin, oleic acid, "recovered grease" (p. 1116), mineral oil, etc.

In order to satisfy the large demand for dégras, frequently skins are worked simply for its production, being oiled and pressed until not a rag is left. Dégras thus prepared must still be considered genuine.

Both sod oil and dégras contain considerable quantities of water, which are held in suspension in the form of an emulsion. The emulsifying body is due, according to *Jean*, to the presence of a "rosinous substance" formed during the oxidation of the oil.

This "rosinous substance" is an acid, has a brown colour, melts at 65°-67° C., dissolves in alkali, but is not precipitated by common salt from its alkaline solutions, is insoluble in water. soluble in alcohol and ether, but *insoluble in petroleum ether*.

Simand described the same substance under the name "*dégras-former*." This "rosinous substance," or "*dégras-former*," is an oxidation product (cp. p. 368), and most likely belongs to the class of oxidised acids. In *Fahrion's*[3] opinion the "*dégras-former*" is a mixture of hydroxylated (oxidised) acids and of their anhydrides.

It is desirable that the use of such unscientific names as "dégras-former," "rosinous substance," should be discontinued.

Most sod oils and dégras contain *unsaponifiable substances* due to the unsaponifiable matter originally contained in the marine animal oils used.

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[1] Schill and Seilacher have patented two methods for preparing artificial dégras by blowing blubber oils with air, or by treating with oxygenated water.

[2] Of course, only very low qualities of tallow or waste fats will be used for this purpose. According to Eitner (*Der Gerber*, 1890, 145), fish stearine obtained from whale oil or from Japan fish oil is very extensively employed, as the rank fishy odour which persistently adheres to this stearine renders it almost useless for soap-making, etc

[3] *Journ. Soc. Chem. Ind.* 1891, 558.

The proportion of *free fatty acids* in sod oils varies greatly; their amount, however, does not affect the quality.

The *specific gravity* of dehydrated dégras is of course higher than that of the oils from which it is prepared, it varies from 0·945 to 0·955; the specific gravity of dégras containing water approaches 1·00. If the dehydrated dégras has a lower specific gravity than 0·920, admixture of mineral oil may be suspected.

An examination of several marine animal oils, according to *Livache's* method (p. 306), proved, in satisfactory agreement with practical experience, that the oils that are best suited for the production of dégras absorb the greatest amount of oxygen. The amounts of oxygen absorbed by skins have been given p. 309. It will be gathered that whale oil is the most suitable oil, whereas sperm oil is almost useless.

The following table, due to *Eitner*,[1] is instructive, as showing the difference between oils and their corresponding sod oils:—

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[1] *Der Gerber*, 1893, 257.

[Table

Name of Oil.	Specific Gravity.		Refractive Index.		Fatty Acids Insoluble in Petroleum Ether.		Acid Value.		Saponification Value.		Acetyl Value.[1]		Iodine Value.	
	Original Oil.	Dégras.	Original Oil.	Dégras.	Original Oil.	Dégras.	Original Oil.	Dégras.	Original Oil.	Dégras.	Original Oil.	Dégras.	Original Oil.	Dégras.
					Per cent.									
Shark liver oil	0·9158	0·9212	1·4735	1·4752	0·91	1·70	7·0	8·4	157·2	143·2	45·0	45	90	82·4
Seal oil	0·9258	0·9465	1·4760	1·4790	2·70	14·41	6·1	26·1	193·8	190·5	25·6	47·8	96·5	68·4
Mixed fatty acids from seal oil	0·9354	0·9473	...	...	3·0	15·51	...	...	...	...	...	...	...	...
Cod liver oil	0·9274	0·9836	1·4755	1·4780	0·87	19·40	13·6	28·3	187·9	183·4	19·4	28·3	14·8	100·5
Mixed fatty acids from cod liver oil	0·9375	0·9612	...	...	1·21	18·44	...	...	...	...	...	...	...	...
Whale oil	0·9270	0·9423	1·4755	1·4758	3·44	6·19	10·6	10·6	190·4	181·5	14·0	22·0	85	71

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[1] These numbers stand in need of confirmation, having been determined by Benedikt and Ulzer's method.

EXAMINATION OF SOD OIL AND DÉGRAS

1. **Determination of Water.**—5 grms. of the sample are mixed with a sufficient quantity of sand to give a solid and nearly dry mass. This is dried at 110° C. According to *Fahrion*[1] this method gives erratic results. Also *Hopkins, Coburn,* and *Spiller*[2] do not consider this a satisfactory method. The method they propose, viz. to allow rolls of filter paper to absorb the sod oil or dégras and to dry in a test-tube with a small hole blown in the bottom so as to be able to draw a current of air through it at 100° C. by means of a suction pump, and to take the loss of weight as moisture, cannot be an accurate one, as oxidation must take place.

French dégras contains, as a rule, 15-25 per cent of water, sod oils from 20-40 per cent (cp. tables below).

2. **Ash.**—This is determined in the usual manner.[3] If the ash has an alkaline reaction, pointing to the presence of soap in the dégras, the amount may be determined by boiling the ash with water, filtering and titrating the filtrate with standard acid.

French dégras contains but a few hundredths per cent of ash, sod oil as much as 3 per cent. The ash should be examined for iron, as iron in dégras is apt to stain the leather.[4]

3. **Mineral Acids.**—A preliminary test is made with litmus paper. If the dégras is found acid, the sample is boiled out with water, and the aqueous layer is titrated with standard alkali, using methyl-orange as an indicator.

Schmitz-Dumont drew attention to the possible presence of soluble fatty acids. He advises to exhaust the aqueous solution with ether. It may be more expeditious to titrate the mineral acids as described, then to add phenolphthalein, and to again titrate until the solution becomes pink.

4. **Fatty Matter.**—The sample is exhausted repeatedly with petroleum ether, and the dissolved fatty matter determined as described p. 150. The insoluble portion consists of water, soap, and hide fragments. The latter are determined by washing the insoluble portion with water and then with alcohol. The residue so obtained is weighed, incinerated, and weighed again. The difference between the two weights gives approximately the amount of hide fragments.

5. **Unsaponifiable Matter.** — This is recovered and examined according to the methods described, Chap. IX. p. 370. If the amount of unsaponifiable matter exceeds 3 per cent, calculated on the anhydrous dégras, adulteration with hydrocarbons, or wool grease (cp. p. 1116), or distilled grease (cp. p. 1119), must be suspected.

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[1] *Zeit. ang. Chem.* 1891, 172.

[2] *Journ. Amer. Chem. Soc.* 1899, 291.

[3] According to *Villon*, a syrupy solution of magnesium chloride is extensively used for mixing with dégras. 20 per cent of this concentrated solution may be added without being detected by the appearance of the dégras or by an abnormal proportion of water.

[4] *Simand* states that as little as 0·05 per cent of ferric oxide has an injurious action. Addition of 500 c.c. of one per cent oxalic acid solution to 100 kg. of dégras is said to remedy this defect.

The detection of cholesterol is not sufficient proof for the presence of *wool grease* or *distilled grease*, as fish and liver oils contain no table proportions of this alcohol; but the appearance of a green fluorescence would point to the presence of isocholesterol and inferentially to that of wool grease or of distilled grease. Raw wool grease not being completely saponified by means of the half-normal alcoholic potash, part of its waxes passes into the unsaponifiable portion. If on saponifying the latter, under pressure, or with sodium alcoholate, a definite saponification value is obtained, the presence of wool wax must be suspected. From the saponification value the quantity of wool wax may be approximately calculated; or the cholesterols in the unsaponifiable matter may be converted into their acetates (see p. 377).

6. **Oxidised Acids.**—These are determined by *Fahrion's* method described p. 368.

A sample may be considered as pure if it yields at least 12 per cent of oxidised acid, calculated to a dégras containing 20 per cent of water. Good samples contain higher proportions of oxidised acids.

7. **Free Fatty Acids.**—These are determined in the usual manner (p. 277). The free fatty acids are usually calculated to oleic acid. The fatty matter obtained from dégras contains, as a rule, 15-20 per cent of free fatty acids.

Jean gives the following analyses of seven samples of dégras :—

		1	2	3	4	5	6	7
Water .	per cent	18·90	14·84	12·93	28·90	19·20	5·39	8·90
Ash . . .	,,	0·25	0·13	0·55	0·70	0·07	0·25	1·21
Hide fragments .	,,	0·30	0·30	0·09	0·58	0·27	...	1·59
Oils . . .	,,	69·71	74·65	80·00	66·93	75·66	84·87	72·15
Unsaponifiable .	,,	6·84	6·05	...	...	...	...	...
Oxidised acids .	,,	4·00	4·05	5·81	3·52	4·80	9·46	16·15

The following table gives *Simand's* analyses of some specimens of dégras and of sod oil :—

	Oxidised Acids.	Melting Point of Fatty Acids.	Soap.	Original Dégras.	
				Hide Fragments.	Water.
	Per cent.	°C.	Per cent.	Per cent.	Per cent.
French dégras, anhydrous No. 1	19·14	18·0-28·5	0·73	0·07	16·5
,, ,, ,, 2	18·43	28·5-29·0	0·49	0·12	20·5
,, ,, ,, 3	18·10	31·0-31·5	0·68	0·18	12·0
Sod oil ,, ,, 1	20·57	33·5-34·0	3·95	5·7	35·0
,, ,, ,, 2	18·63	27·5-27·0	3·45	5·9	28·0
,, ,, ,, 3	17·84	28·0-28·5	3·00	4·5	30·5

The quantitative reactions, such as the determination of saponification and iodine values, have been used by several chemists in the examination of dégras: it should, however, be borne in mind that they have but little discriminative value in this case. A large quantity of mineral oils is more readily detected by the determination and examination of unsaponifiable matter than by the saponification value.

An exhaustive examination of a number of dégras, using the quantitative reactions, has been made by *Ruhsam*.[1] His results are given in the following table :—

1	2	3	4	5	6	7	8	9	10	11
		Iodine Value.				Acid Value.		Saponification Value.		
No. of Sample.	Water.	Original Dégras.	Anhydrous Dégras.	Insoluble Fatty Acids.	Acetylated Fatty Acids.	Original Dégras.	Anhydrous Dégras.	Original Dégras.	Anhydrous Dégras.	Mgrms. of KOH per gra[illegible] corresponding to Lactone
	Per cent.									
1	19·1	60·4	74·7	70·5	73·1	30·5	37·7	...	...	38·[illegible]
2	12·9	55·9	64·2	58·6	52·7	63·3	72·7	96·2	110·4	2[illegible]·7
3	12·4	67·8	77·4	75·4	90·4	35·2	40·2	97·0	110·7	43·4
4	15·9	65·9	78·4	70·2	66·6	42·1	50·1	113·4	134·8	30·8
5	16·4	65·0	77·8	78·5	76·2	44·1	52·7	114·9	137·4	22·4
6	11·5	67·8	76·6	76·5	75·7	57·4	64·9	96·3	108·8	53·8
7	13·9	83·3	96·7	95·9	88·9	...	...	...	...	33·1
8	17·3	69·2	83·7	93·4	102·7	23·9	28·9	83·4	100·8	100·4
9	16·6	67·5	80·9	...	...	43·4	52·0	117·8	141·2	...
10	5·3	70·5	74·4	79·3	73·0	51·2	54·1	118·6	125·2	30·7
11	...	127·7	127·7	142·3	127·4	..	...	...	163·8	31·4
12	...	...	126·7	106·0	101·9	...	...	...	186·0	53·9
Mean of 1-10	...	...	78·5	77·6	77·7	...	50·4	...	121·2	42·4

The samples 1-9 are French artificial dégras. No. 10 is a so-called "emulsion fat," No. 11 a moëllon prepared by *Ruhsam* from whale oil No. 12. The acetyl values given in the original paper have been omitted here for the reasons given p. 276.

Schmitz-Dumont's figures for a number of dégras and commercial products giving high proportions of unsaponifiable matter are contained in the following table :—

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[1] *Journ. Soc. Chem. Ind.* 1892, 639.

[TABLE

No.			Water.	Ash.	Insoluble in Petroleum Ether.	Fatty Matter.	Unsaponifiable Matter.	Oxidised Acids.	Anhydrous Fat.		
									Acid Value.	Saponific. Value.	Iodine Value.
			Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.			
1		Dégras	13·31	0·32	0·31	86·1	3·1	11·03	108·0	185·8	69
2		,,	10·05	0·18	0·24	89·5	3·4	14·13	119·0	188·0	52·8
3		,,	10·24	0·28	0·28	89·2	1·0	1·49	104·0	181·8	70·7
4		,,	8·49	0·06	0·31	91·1	0·91	9·25	34·5	208·5	106·0
5		,,	17·33	0·27	0·14	82·3	2·51	0·95	29·2	206·0	122·0
6		,,	10·59	0·20	0·10	89·1	3·1	10·93	112·0	181·2	63·9
7		,,	1·53	0·70	0 04	97·7	1·85	16·17	112·0	170	62·5
8		Moëllon, pure	18·45	0·07	0·09	81·4	2·04	11·65	25·7	215·5	89·1
9		,,	19·88	0·03	0 46	79·63	0·45	1·46	47·4	214·0	115·0
10		Moëllon-dégras	11·65	0·63	0·98	86·74	3·27	2·01	17·4	196·7	126·0
11		Oxidised blubber oil	10·43	0·50	0·21	88·86	1·44	1·61	17·0	192·3	129·0
12		Oxidised emulsion fat	7·45	0·41	0·08	92·1	2·72	9·74	17·0	196·3	107·8
13	Of French origin	Dégras	13·88	0·14	0·22	86·8	40·6	4·06	35·0	99·8	52·9
14		,,	14·16	0·58	0·97	84·3	18·9	3·73	32·4	137·4	80·6
15		,,	25·46	0·07	1·25	73·22	14·29	5·99	33·0	206·4	101·8
16		,,	18·79	0·46	0·31	80·44	23·61	5·33	31·0	135·4	72·3
17		Dégras-moëllon	15·79	0·05	0·22	83·94	28·1	1·84	40·5	113·2	72·1
18		Dégras	7·59	0·26	0·38	91·8	33·12	3·39	39·7	93·0	49·9
19		"Mutton dégras"	16·49	0·31	0·74	82·5	8·5	5·51	39·4	194·0	104·5
20		Dégras moëllon	14·29	0·29	0·38	85·04	14·1	4·96	38·4	180·0	102·0
21		Dégras	20·37	0·08	0·45	79·1	40·3	2·95	24·0	86·0	49·5
22		,,	30·29	0·25	0·22	69·24	2·23	6·55	54·6	201·0	90·0
23		Fat from sod oil	..	..	..	100·0	0·71	16·84	71·3	234·0	61·0

Similar analyses, published by *Tortelli*, are reproduced in the following table :—

[TABLE

No.		Specific Gravity at 18° C.	Water.	Ash.	Insoluble in Petroleum Ether.	SO$_3$.	Unsaponifiable Matter.	Oxidised Acids		Acid Value of		Saponification Value of		Iodine Value of	
			Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	in Original Substance.	in Anhydrous Substance.	Original Substance.	Anhydrous Substance (calculated).	Original Substance.	Anhydrous Substance (calculated).	Original Substance.[1]	Anhydrous Substance (calculated).
1	Natural dégras from chamoisin ;	1·0025	31·13	1·83	5·07	0·47	2·36	18·03	26·38	35·75	51·75	155·0	221·0	35·7	52·3
2	,, ,, ,,	0·9993	39·60	1·79	5·18	0·20	1·26	14·09	23·44	25·08	41·72	144·0	239·0	34·0	56·4
3	Fish oil, used in dégras manufacture	0·9172	0·20	0·03	...	0·0	1·30	3·79	3·80	9·39	...	192·3	192·3	139·7	139·7
4	Commercial "dégras," German	0·9435	17·74	0·11	0·15	0·0	1·16	9·66	11·77	16·64	20·02	172·0	209·0	69·0	83·8
5	,, ,, French	0·9495	18·13	0·32	trace	0·0	19·61	2·03	2·48	22·49	27·46	131·2	160·0	64·1	78·9
6	,, ,, French	0·9445	17·35	0·49	trace	0·03	2·25	6·65	8·04	11·72	14·18	164·0	198·0	95·6	115·6
7	,, ,, French	0·9466	20·78	0·38	trace	0·04	1·88	9·44	11·92	11·55	19·62	160·0	193·0	53·8	65·3
8	,, ,, German	0·9493	22·89	0·60	0·23	0·02	8·75	9·11	11·81	11·83	15·35	126·0	163·4	44·7	58·0
9	,, ,, German	0·9493	21·33	0·55	0·30	0·06	15·77	4·30	5·47	11·49	14·61	105·0	129·0	39·6	50·4
10	,, ,, French	0·9498	21·40	0·10	0·12	0·02	30·56	5·40	6·87	19·29	24·54	95·0	120·9	45·4	57·7
11	,, ,, Belgian	0·9506	22·70	0·08	0·32	0·04	22·26	6·18	7·99	18·77	24·28	92·5	119·2	46·1	59·6
12	,, ,, Belgian	0·9516	10·89	0·31	0·86	0·02	17·59	4·90	5·50	12·63	14·27	136·0	152·6	50·2	50·7

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[1] The iodine value was determined in the substance containing water.

Hopkins, *Coburn*, and *Spiller*[1] have examined twelve American sod oils. The maxima and minima are given in the following table. The numbers are calculated in terms of anhydrous sod oil :—

	Water.	Ash.	Mineral Acid in terms of KOH.	Oil, etc., soluble in petroleum spirit.	Soap, etc., soluble in Alcohol.	Hide fragments.	Unsaponifiable Matter.	Oxidised Acids.	Free Fatty Acids in terms of KOH.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Minimum	1·01	0·05	1·13	56·62	0·68	0·15	0·37	1·09	32·65
Maximum	40·61	1·045	91·51	96·60	8·81	2·99	42·62	26·44	34·26

ARTIFICIAL DÉGRAS

It has been pointed out already that pure moëllon is, as a rule, mixed with tallow and untreated oils, so that these admixtures cannot be regarded as adulterants. Frequently even vegetable oils are admixed with dégras. A large number of artificial dégras are now being prepared by blowing fish, liver, and blubber oils[2] with air in the manner in which "blown oils" are prepared, thus imitating the natural process of oxidation the oils appear to undergo when skins are converted into chamois leather. *Baron*[3] prepares an artificial dégras by blowing neutral wool fat and cod liver oil or whale oil, finally treating the mixture and hydrogen peroxide and water. The product forms an emulsion with water.

"*Corroïne*," another artificial dégras, is stated to consist of a mixture of vaseline and wool fat, emulsified with water.[4]

6. Stuffing Greases

Stuffing greases are either of similar composition to that of an artificial dégras, or consist of a mixture of horse fat, skin grease, bone fat, and tallow, or of tallow and fish stearine, etc. Some stuffing greases are nothing else than distilled grease stearine (p. 1119) or even "recovered grease" (p. 1116). Other stuffing greases again contain a considerable proportion of hydrocarbons of high specific gravity, as also of mineral waxes.

7. Garbage Fats—Sewage Fats

Waste fats from sewage water, abattoirs, etc., contain fatty matter both in the form of unsaponified fat, and in the form of soap.

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[1] *Journ. Amer. Chem. Soc.* 1899, 291.

[2] Cp. Schill and Seilacher, footnote 1, p. 1121.

[3] *Rev. Chim. Ind.* 1897, 225.

[4] *Journ. Soc. Chem. Ind.* 1895, 815.

Up to recently no attempt had been made to recover these fats, as sanitary considerations demand their speedy removal from the households, etc., into sewage works, it being considered more economical to run them to waste. During the last few years, however, when prices of fatty matters were high, experiments have been made both in the United States and on the Continent with a view to recovering the fatty matter. Various patents have been taken out to protect processes of this kind. As an example may be mentioned German Patent 135,313,[1] which has been carried out on a large scale. The sewage water is treated with a mineral acid in a similar manner as is done in the recovery of wool grease, the separated fatty matter is pressed, dehydrated, and extracted with solvents. A specimen of extracted fat had the following composition:—

Free fatty acids	70·8 per cent.
Neutral fat	17·6 ,,
Unsaponifiable matter . . .	11·6 ,,

Judging from the composition of this fat, it is evident that its recovery cannot pay the expenses of the process,[2] unless, indeed, the recovery of the fat form an integral part of the sewage disposal process. Some exaggerated statements made as to the value of some of these recovery processes must therefore be accepted with the greatest reserve, especially in view of the present low prices of natural oils and fats.

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[1] Cp. also U.S.P. 709,384.

[2] Cp. Lewkowitsch, *Journ. Soc. Chem. Ind.* 1903, 70.

APPENDIX

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BETWEEN the acids of the linolic series and of the linolenic series there must be interposed :—

ACIDS OF THE CHAULMOOGRIC SERIES, $C_nH_{2n-4}O_2$.

These acids differ from the isomeric acids of the linolic group by being cyclic compounds, and containing only one pair of doubly-linked carbon atoms. Hence they absorb two atoms only of bromine or iodine.

Several homologous acids belonging to this series occur in chaulmoogra oil, the oil contained in the seeds from *Taraktogenos Kurzii*, King (*Power* and *Gornall*).[1] Hitherto one of these acids, *chaulmoogric acid*, has been prepared in the pure state.

CHAULMOOGRIC ACID, $C_{18}H_{32}O_2$

This acid has been obtained from the mixed fatty acids of chaulmoogra oil by crystallisation from petroleum ether. The acid crystallises in glistening leaflets, melting at 68° C., and boiling at 247°-248° C. under a pressure of 20 mm. Like the oil from which it is derived, the acid is optically active. $[\alpha]_D = +56°$.

On treating chaulmoogric acid with hydrobromic acid in glacial acetic acid, bromodihydrochaulmoogric acid, $C_{18}H_{33}BrO_2$ (melting at 36°-38° C.) is formed. This acid is optically inactive. On reducing this acid with zinc dust and alcohol, dihydrochaulmoogric acid, $C_{18}H_{34}O_2$ (of the melting point 71°-72° C. and boiling point 248° C. under a pressure of 20 mm.) is obtained. This acid is a saturated acid, and is also optically inactive. The same acid is obtained when chaulmoogric acid is treated with hydriodic acid and phosphorus; a hydrocarbon, chaulmoogrene, $C_{18}H_{34}$ (boiling point 193°-194° C. at 200 mm. pressure) is formed as a by-product. Chaulmoogric acid is not attacked by fusing caustic alkalis even at 300° C. On oxidising chaulmoogric acid with potassium permanganate in the cold, dihydroxydihydrochaulmoogric acid, $C_{18}H_{32}(OH)_2O_2$, is produced. If an excess of permanganate be used, formic acid and two dibasic acids of the formula $C_{15}H_{28}(CO_2H)_2$ and $C_{15}H_{28}O(CO_2H)_2$ are obtained.

On allowing sodium to act on chaulmoogric acid in amyl alcohol solution at the boiling point of the latter, chaulmoogryl alcohol, $C_{18}H_{33}OH$

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[1] *Proceedings Chem. Soc.* 1904, June.

(melting point 36° C.; $[\alpha]_D = +58{\cdot}4°$), and chaulmoogryl chaulmoograte, $C_{17}H_{31}.CO_2.C_{18}H_{33}$ (melting point 42° C.) are obtained, together with unchanged chaulmoogric acid.

The *methyl-ester* melts at 22° C., boils at 227° C. (corr) under a pressure of 20 mm., has a specific gravity of 0·9119 at 25° C. (water at 25° C. = 1), and the specific rotation $[\alpha]^{15°}_{D} = +50°$ in chloroformic solution.

The *ethyl-ester* is a colourless oil of the boiling point 230° C. at a pressure of 20 mm.; it has the specific gravity 0·9079 at 15° C. (water at 16° = 1), and the specific rotation $[\alpha]^{20°}_{D} = +50{\cdot}7°$.

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Add to the list—

Fatty Acid.	Hydroxylated Acid.
Chaulmoogric acid .	Dihydroxy-dihydro-chaulmoogric acid.

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Two dibasic acids of the formulæ $C_{15}H_{28}(CO_2H)_2$ and $C_{15}H_{28}O(CO_2H)_2$ (melting point 128° C.) have been obtained on oxidising chaulmoogric acid with potassium permanganate.

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To the list of oils having a definite rotatory power, there must be added (1) *stillingia oil* (Chap. XIV. p. 472), which gives in a 200 mm. tube the rotation of − 6° 45′, and (2) *chaulmoogra oil* (see p. 693 and p. 1136), the specific rotation of which is $[\alpha]^{15°}_{D} = +52°$. These observations qualify the remarks made in the third paragraph on page 210.

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Fendler[1] recently examined the seeds of *Aleurites Moluccana* from the Cameroons. The kernels contained 6·3 per cent of water and 64·4 per cent of oil. The oil obtained by extraction with ether has a yellow colour and an acrid smell. Its specific gravity at 15° is 0·9254; solidifying point, − 15°; saponification value, 194·8; iodine value, 114·2; and Reichert-Meissl value, 1·2. The solidifying point of the fatty acids is 15·5° C., and their melting point 18° C.

On comparing these numbers with those given for candle nut oil (p. 468), it will be observed that the iodine value is considerably lower. This is all the more surprising, as *Fendler* states that the oil dries quickly when spread in a thin layer.

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[1] *Zeit. Unters. d. Nahrungs u. Genussm.* 1903. 1025.

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BURDOCK OIL—BUR OIL

French—*Huile de bardane.* German—*Klettensamenöl.*
Italian—*Olio di bardana.*

This oil is obtained from the seeds of *Lappa Minor* (*Arctium Lappa*). The seeds are of the size of linseed, but have a more spherical form. One litre of seeds obtained from the Charkoff district[1] weighs 641 grams. They consist of 46·4 per cent of husks. The seeds contain 14·8 per cent of oil.

The pressed oil is pale yellow. It has an odour resembling that of linseed oil, and a somewhat bitter taste. The specific gravity of the oil at 17° C. is 0·9255; its saponification value, 196·6; its iodine value, 153·6; and its Reichert-Meissl value, 0·95. The iodine value of the insoluble fatty acids is 162. The acid value of the specimen examined by *Lidoff*[1] was 2·0.

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[1] A. P. Lidoff, *Chem. Zeit. Rep.* 1904, 161.

[TABLE

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LESSER KNOWN SEMI-DRYING OILS

Source.	Yield Per cent.	Specific Gravity.	Saponification Value.	Iodine Value.	Hehner Value.	Refractive Index.	Neutralisation Value of Fatty Acids.	Solidifying Point of Fatty Acids. °C.	Melting Point of Fatty Acids. °C.	Iodine Value of Mixed Fatty Acids.	Refractive Index of Fatty Acids.	Observer.
Xantium strumarium[1] .	28	...	...	...	...	...	...	...	...	147·9	...	Fokin[5]
Galeopsis ladanum[2] .	40·4	0·922 (at 20° C.)	...	...	...	...	...	...	...	147·0	...	,,
Leonurus cardiaca[1] .	23	0·923 (at 20° C.)	...	...	...	...	...	...	...	133·7	...	,,
Tilia parvifolia[1] . .	26·6	0·926 (at 20° C.)	184·8	123·9	95·1	...	197·0	9-18	17-26	130·3	...	,,
Euonymus verrucosus[1] [3].	43·64	0·959 (at 20° C.)	...	...	...	...	198·5	22-23	...	110·6	...	,,
Delphinium elatum[1] [4] .	36·6	0·921 (at 20° C.)	...	...	...	72° in Butyrorefractometer	191·8	...	...	108·2	56·6 in Butyrorefractometer	,,

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[1] Amongst the liquid fatty acids linolic acid is present; linolenic acid is absent.

[2] Amongst the liquid fatty acids linolic and linolenic acids are present.

[3] Specific gravity of the mixed fatty acids, 0·912. The Reichert-Meissl value is stated to exceed 4.

[4] Specific gravity of the mixed fatty acids, 0·8915 at 20° C.

[5] *Chem. Revue*, 1904, 70.

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The seeds of *Rhus glabra*, freed from husks, yield to ether 9·1 per cent of a light yellow oil. The oil has a pleasant taste and a characteristic odour. The specific gravity at 0° C. is 0·9312, and at 20° C. 0·9203; saponification value, 200; iodine value, 85·96 to 87·86. The refractive index at 0° C. is 1·48821, and at 15° C. 1·48228.

The husks yielded to ether 8·5 per cent of a black viscous oil of specific gravity 0·9412 at 20° C., and 0·933 at 35° C. This oil has the saponification value 179·7, and the iodine value 87·2.[1]

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The American whalers still "try," to a large extent, the blubber on board ship and deliver the crude oil into the refineries in New Bedford, Mass., on the east coast, and San Francisco, on the west coast.

The "right whale" oil is of better quality than the "southern whale" oil. The "finner whale" oil is of still lower quality. Hence the finner whale was formerly neglected by the whalers, but at present even this kind of whale is eagerly pursued by them along the coast of Norway and Newfoundland, as also to a smaller extent on the Asiatic coast of Russia, and the coast of Japan.

Besides the whales named, other kinds of whales, such as the "orca" or "killer" whale, the "beluga" or white whale, are caught, especially by the American whalers, and the blubbers are rendered for whale oil.

The average yield of oil obtainable from the different species of whales is given in the following table:—

Kind of Whale.	Yield in Barrels of 31·5 gallons.
Right whale, Pacific	25 to 250
Right whale, Atlantic	25 ,, 150
Bowhead whale	30 ,, 250
Humpback whale, Pacific	10 ,, 110
Humpback whale, Atlantic	10 ,, 100
Finback whale, Pacific	10 ,, 70
Finback whale, Atlantic	20 ,, 60
Californian gray whale	15 ,, 60
Orca or killer whale	1 ,, 6
Beluga or white whale	1 ,, 3

The total production of whale oil amounts at present to 3 million gallons per annum; of these 900,000 are produced by the Norway fisheries, 750,000 by the United States fisheries, and the remainder by Scotland, Russia, Newfoundland, Japan, and other countries.

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[1] Frankforter and Martin, *Amer. Journ. Pharm.* 76, 151.

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According to *Power* and *Gornall*[1] chaulmoogra oil is obtained from the seeds of *Taraktogenos Kurzii*, King, a plant indigenous to Burmah. The oil obtained by expression had the specific gravity 0·951 at 25° C., and 0·940 at 45° C.; melting point, 22°-23°: saponification value, 213; and iodine value, 103·2. The oil is optically active, and has the rotation $[\alpha]_D^{15^\circ} = +52^\circ$. The acid value of the sample was 23·9. (Since the seeds contain a hydrolytic enzyme, the high acid value of the freshly expressed oil may be explained by hydrolysis having taken place whilst the seeds were crushed.—J.L.) (Cp. Chap. II. p. 49.)

The mixed fatty acids melt at 44°-45° C., and have the neutralisation value, 215; iodine value, 103·2; the optical rotation is $[\alpha]_D = +52{\cdot}6^\circ$ in chloroformic solution.

Amongst the fatty acids palmitic acid was identified. The fatty acids consist chiefly of homologous acids belonging to the "chaulmoogric series" $C_nH_{2n-4}O_2$. These acids differ from the isomeric acids of the linolic series (Chap. III. p. 111), in that they are cyclic compounds, and contain only one pair of doubly-linked carbon atoms. The highest of th~~o~~ese homolog~~ou~~ues, chaulmoogric acid, $C_{18}H_{32}O_2$, was isolated in the pure condition. Undecylenic and hydroxylated acids were proved to be absent. (Cp. also *Schindelmeiser's*[2] description of gynocard oil.)

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According to *Davis* and *M'Lellan*,[3] the roasted cacao beans are best extracted with petroleum ether of boiling point 40° C. to 50° C. The common ether extracts 0·2-0·5 per cent more than petroleum ether, theobromine and some colouring matter being dissolved by the common ether. The following percentages of fat were ascertained in roasted nibs:—

Country.	Fat per cent.
Ecuador, Arriba	54·66
,, other varieties	52·87
Venezuela, East of Caracas	51·33
,, West of Caracas	53·05
Dutch Guiana, Surinam	56·37
Brazil, Para	54·98
,, Bahia	54·33
Africa, West Coast	54·18
West Indies, Trinidad	54·57
,, Grenada	55·30
,, Dominica	56·03
,, Santa Dominigo, Samana	55·38
Jamaica	56·57
Ceylon	53·36

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[1] Power and Gornall, *Proceedings Chem. Soc.* 1904, June.

[2] *Berichte d. d. Pharm. Ges.* 1904, 164.

[3] *Journ. Soc. Chem. Ind.* 1904, 480.

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THE END

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